J. Indian Chem. Soc., Vol. LVII, No. 7, Pp. 667-764
July 1980
CODEN : JICSAH LVII, (7) (1980), 667-764

JOURNAL

OF THE

INDIAN CHEMICAL SOCIETY

Published by The Indian Chemical Society
92, Acharya Prafulla Chandra Road,
Calcutta-700 009

Indian Chemical Society

92, ACHARYA PRAFULLA CHANDRA ROAD, CALCUTTA-700 009.

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Mixed Ligand Complexes of Nickel(II) with Salicyclideneamino-carboxylic Acids and N-donor Ligands

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Manuscript received 13 November 1979, accepted 20 December 1979

Mono- and diamine adducts of salicylidenaminocarboxylate complexes of nickel (II) have been prepared and analysed by elemental, molar conductance, magnetic moment, infra-red and electronic spectral analyses. The compounds have the compositions NiSA.L_2 (where L = monoamines like pyridine (Py), α-picoline (α-pic), γ-picoline (γ-pic), quinoline (Q) and triethylamine (Et_3N) and NiSA.L′.nH_2O (where L′ = ethylenediamine (en), (*o*-phenylenediamine (*o*-pd), *o*, *o*′-bipyridyl (bp) and *o*-phenanthroline (*o*-phen) with SA^{--} = salicylideneglycinate (Sg^{--}) or salicylideneanthranilate (Sa^{--}). All the compounds are found to be dimeric octahedral complexes using a bidentate carboxylic bridge.

THIS work has been undertaken as a part of our systematic work on the salicylideneamino-carboxylate complexes of bi- and trivalent metal ions and their adducts with various heterodonors. Such compounds have many interesting structural, magnetic, spectroscopic and other properties[1-3]. Theriot *et al*[1] have prepared the diaquosalicylideneglycinatonickel(II) and reported its composition, magnetic moment and electronic spectrum. This paper reports the properties of the compounds formed by the reaction of various monoamines viz. pyridine (py), α-picoline (α-pic), γ-picoline (γ-pic), quinoline (Q), triethylamine (Et_3N) and diamines viz. ethylenediamine (en), *o*,*o*′-bipyridyl (bp), *o*-phenylenediamine (*o*-pd) and *o*-phenanthroline (*o*-phen) with the Ni(II) complexes of salicylideneglycine (H_2Sg) and salicylideneanthranilic acid (H_2Sa).

Experimental

Materials: All chemicals used were of pure/AnalaR grade. Methanol used as solvent was purified by standard method[4]. The compounds were prepared in the same way as the corresponding compounds of Cu(II) described elsewhere[3].

Methods: Magnetic susceptibility of the compounds have been determined by Gouy method from solid specimen using $CoHg(NCS)_4$ and $CuSO_4.5H_2O$ as standards. Molar conductance has been determined in $10^{-3}M$ methanolic solutions using Phillips conductivity bridge. Infra-red spectra of the compounds have been recorded between 4000 to 600 cm^{-1}. Similarly electronic spectra have been recorded in the region 50,000 cm^{-1} to 6,000 cm^{-1}.

Results and Discussion

Results of analysis and other physical data are recorded in Table 1. Molar conductance data (<13 mhos cm^2 $mole^{-1}$) indicate non-electrolytic nature of the compounds.

The TIP corrected magnetic moments are found to be in the range 3.13-3.35 BM per nickel atom. The values are consistent with high-spin octahedral configuration for the Ni(II) ion. The spin-orbit coupling constant (λ) lies in the range 267-309 cm^{-1} against free ion value (λ_0) of 324 cm^{-1}[4,5]

The compounds contain modified infra-red absorptions of both the starting complexes [salicylideneglycinatonickel(II) and salicylideneanthranilatonickel(II)] and the heteroligands indicating the formation of mixed ligand complexes. The ν(N-H) vibrations are clearly observable from the spectra of the ethylenediamine and *o*-phenylenediamine adducts within 3220-3300 cm^{-1}. The bipyridyl adduct of salicylideneglycinatonickel II) has a broad band at 3550 cm^{-1} which may be due to the ν(O-H) vibration of the lattice water molecule. The ν(C=N) vibrations of the azomethine groups appear at 1602-1630 cm^{-1} either separately or mixed with other vibrations in that region. This is at a lower energy region than those of the free Schiff-base ligands. The ν(C-O) (phenolic) band occurs at 1310-1330 cm^{-1} which is about 20-40 cm^{-1} higher than that due to the free Schiff-bases indicating monodentate nature of the phenolic oxygen atom[7]. For a bidentate or bridging phenolic group, this vibration occurs at a considerable higher frequency[8],[9], ~1550 cm^{-1}. The asymmetric and symmetric stretching vibrations of the carboxylate groups, $\nu_{as}(COO^-)$ and ν_s (COO^-), occur at 1570-1590 and 1472-1485 cm^{-1}

TABLE 1— ANALYSES, MELTING POINT, MAGNETIC MOMENT, MOLAR CONDUCTANCE AND ELECTRONIC ABSORPTION SPECTRAL DATA

Compound	Colour	Form	Analyses[a] %Ni	Analyses[a] %N	μ_{eff} (B.M.)	Λ_M (mhos cm^2 mole^{-1})	Ligand field bands in methanol (in cm^{-1}) ν_1^c	ν_2^c	ν_3^a	$^a_2$
$[NiSg(Py)_2]_2$	Light-green	Crystalline	15.0 (14.90)	10.6 (10.66)	3.26	6.5	11,000 (39.4)	17,545 (31.6)	(17,525)	(28,250)
$[NiSg(\alpha\text{-pic})_2]_2$	Green	-do-	14.0 (13.91)	10.0 (9.95)	3.31	7.6	10,925 (16.3)	17,390 (25.6)	(17,355)	(28,250)
$[NiSg(\gamma\text{-pic})_2]_2$	Bluish-green	Micro-crystalline	13.8 (13.91)	10.1 (9.95)	3.13	6.8	10,930 (14.5)	17,390 (18.6)	(17,125)	(28,400)
$[NiSgQ_2]_2$	Green	Crystalline	11.6 (11.89)	8.5 (8.51)	3.13	8.0	9990 (21.2)	15,505 (31.6)	(15,535)	(25,650)
$[NiSg(Et_3N)_2]_2$	Light-green	Micro-crystalline	12.9 (13.41)	9.6 (9.60)	3.18	10.5	9970 (21.2)	15,670 (25.5)	(15,610)	(25,515)
$[NiSa(Py)_2]_2$	Yellowish-green	Crystalline	12.9 (12.88)	9.2 (9.21)	3.35	7.8	11,050 (25.7)	17,095 (37.6)	(17,110)	(27,050)
$[NiSa(\alpha\text{-pic})_2]_2$	Yellow	-do-	11.8 (12.13)	8 8 (8.68)	3.34	8.7	11,000 (16.5)	17.545 (15.3)	(17,525)	(28,250)
$[NiSa(\gamma\text{-pic})_2]_2$	Light-yellow	Micro-crystalline	12.1 (12.13)	8.7 (8.68)	3.27	6.7	10,850 (16.7)	16,050 (22.3)	(16,080)	(27,175)
$[NiSaQ_2]_2$	Yellowish-green	Crystalline	10.3 (10.56)	7.6 (7.56)	3.26	8.7	10,000 (34.4)	16,530 (39.5)	(16,480)	(26,420)
$[NiSa(Et_3N)_2]_2$	Light-green	Micro-crystalline	11.5 (11.75)	8 5 (8.40)	3.36	10.8	9970 (27.3)	15,870 (30.8)	(15,845)	(25,430)
$[NiSg\ en]_2$	Brick-red	Crystalline	19.5 (19.85)	14.0 (14.20)	3.19	11·6	11,000 (15 6)	17.545 (16.6)	(17,528)	(28,260)
$[NiSg(o\text{-pd})]_2$	Blue	Crystalline	16.7 (17 08)	12.1 (12.22)	3.21	12.3	10,500 (25.6)	16,815 (30.5)	(16,800)	(27,290)
$[NiSg(bp)]_2.2H_2O$[b]	Green	Micro-crystalline	14.2 (14.32)	10.1 (10.25)	3.29	8.5	10,600	17,390	(17,020)	(29,285)
$[NiSg(o\text{-phen})]_2$	Light-green	Crystaline	14.0 (14.12)	9.6 (10.10)	3.33	9.5	10,985 (35.9)	17.515 (30.0)	(17,490)	(28,200)
$[NiSa\ en]_2$	Buff	-do-	15.9 (16.41)	11.8 (11.74)	3.24	11.2	11,020 (10.8)	17,480 (12.4)	(17,450)	(28,050)
$[NiSa(o\text{-pd})]_2$	Light-pink	Micro-crystalline	14.3 (14.47)	10.3 (10.35)	3.23	12.8	10,750 (51.8)	16,385 (58 5)	(16,395)	(25,720)
$[NiSa(bp)]_2$	Yellowish-green	-do-	13.0 (12.94)	9.2 (9 26)	3.27	9.3	10,500 (14.4)	16,815 (19.3)	(16,800)	(27,300)
$[NiSa(o\text{-phen})]_2$	Yellowish-green	Crystalline	11.8 (12.29)	8.6 (8.79)	3.33	7.8	10,500 (46.5)	17,285 (53.8)	(17.245)	(29,546)

a. Figures in parentheses show the calculated values. (ν_2 calculated by procedure of Lever[12], ν_3 calculated by procedures of Lever[12] and Underhill and Billing[13])
b. %H_2O 4.2 (found), 4.39 (calculated).
c. Figures in parentheses are molar extinction coefficients.

respectively with a difference, $\Delta\nu$ (COO$^-$), of 95-105 cm^{-1}. A free ionic carboxylate group[7] usually has a $\Delta\nu$ (COO$^-$) of $\approx$200 cm^{-1}. A monodentate carboxylate group[7] has a difference of 150-180 cm^{-1}, but a bidentate or bridging carboxylate has a much closer difference ($<$120 cm^{-1})[10,11]. Bridging carboxylate groups are, therefore, indicated in the present compounds.

The lowest energy ligand field transition occurs at 9,970-11,765 cm^{-1} which may be taken as ν_1(10Dq) band corresponding to $^3A_{2g} \rightarrow {}^3T_{2g}$ transition of nickel(II) under octahedral symmetry. The ν_2 band corresponding to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition occurs at 15,505-17,545 cm^{-1}. The ν_2/ν_1 ratio ranges between 1.48-1.65 which is close to 1.6 expected for octahedral Ni(II) complexes. In some compounds another band of very low intensity occurs in between these two bands (12,500-13,570 cm^{-1}) which may be due to spin-forbidden $^3A_{2g} \rightarrow {}^1E_g(D)$ transition. The ν_3 band $[^3A_{2g} - {}^3T_{1g}(P)]$ position of the complexes has been calculated from their ν_1 and ν_2 band positions by the procedures of Lever[12] and Underhill and Billing[13]. The calculated value of ν_3 position is within the range 25,450-29,500 cm^{-1}. This band could not be seen separately because it gets masked by intense charge transfer bands in that region. A weak band, usually occurring as a shoulder to the nearby charge-transfer band, is seen in some compounds at 20,600-23,400 cm^{-1} which may be due to spin-forbidden $^3A_{2g} - {}^1T_{2g}(G)$ transition. The Racah parameter (B) has been calculated to be between 565 to 1019. The naphelauxetic parameter (β_{35}) is within 0.62-0.81.

In view of the above analytical, spectral, magnetic moment and other data all the compounds may be inferred to be dimeric and octahedral in

structure containing bidentate carboxylate groups and four monoamine molecules or two diamine molecules in the co-ordination sphere (Fig. 1 & 2).

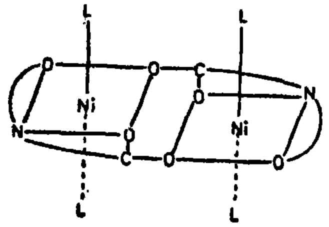


Fig. 1

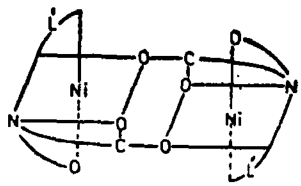


Fig. 2

Acknowledgement

The authors wish to express their gratitude to the Board of Scientific and Industrial Research, Government of Orissa for supporting the research scheme.

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J. Indian Chem. Soc.,
Vol LVII, July 1980, pp. 670-672

Proton Ligand Formation Constants of 1-Amino-2-Naphthol-4-Sulphonic Acid (ANSA)

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Manuscript received 8 August 1979, accepted 30 December 1979

Chelation tendency of 1-amino-2-naphthol-4-sulphonic acid has been worked out and the proton ligand formation constants have been computed using various methods, in 50% aq.-dioxan, at 35° and at ionic strengths of 0.05, 0.1 and 0.2 *M* adjusted by the addition of KNO_3, with the use of Bjerrum-Calvin *p*H-titration technique. Thermodynamic formation constants have been obtained by extrapolation to zero ionic strength.

METAL complexes have been reported to play important part in the biological activity of drugs. A current theory of the drug action centres around the competitive binding[1]. Further cancer formation and its inhibition, both involve chelation. The trace metals present in the body are generally transition metals. These abnormal metals change the behaviour of enzyme systems, by binding with them and replacing the essential metals of these systems ; they also change the structure of the nucleic acid by binding with them. Most of the compounds which cause cancer are also chelating agents. One of the several such compounds is 1-amino.2-naphthol. 4-sulphonic acid. It is a purple coloured sparingly soluble compound in hot water. The structure of the molecule clearly indicates its potentiality for complex formation with metals. The amino-naphthols and their derivatives have been shown carcinogenic, particularly in the bladder cancer[2]. Literature survey indicates that practically no work has been done with this compound describing its complex forming potentiality, except that with Pd(II) and V(V)[3]. Hence it was thought fruitful to work out the avidtiy of this molecule for chelate formation. As the molecule is an acid, its pK^a values will give an idea about the availability of the chelating species (the anion) at the physiological *p*H, 7.3. In this note, the proton ligand formation constants log K_n^H, of ANSA have been calculated in 50% aq.-dioxan medium at 35° and at various ionic strengths with KNO_3. Thermodynamic formation constants have been obtained by extrapolation to zero ionic strength (Fig. 2).

Experimental

All the solutions were prepared by dissolving high purity chemicals in doubly distilled, CO_2 free water. ANSA (B. D. H.) was dissolved in dioxan, while KOH solution was prepared in CO_2-free water and standardised against a standard solution of oxalic acid.

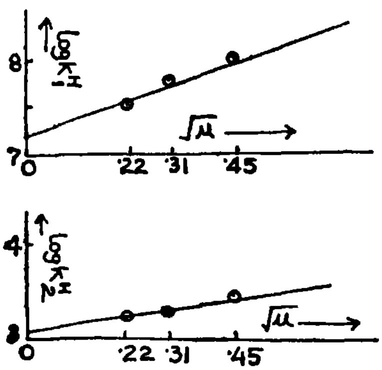


FIG-2

The Bjerrum-Calvin *p*H-titration technique[4], as adopted by Irving and Rossotti[5] was used to determine proton-ligand formation constants of ANSA. The two sets of solutions of (a) nitric acid and (b) nitric acid and ANSA, were prepared such that the total volume was 50 ml and the final concentrations were $1.0\times10^{-2}M$ HNO_3 and 2.0×10^{-3} *M* ANSA in each case. The ionic strength of each of the solution was maintained at 0.05*M*, 0.1*M* and 0.2*M* using KNO_3. The titrant was 0.1*M* KOH and 'Systronics' *p*H-meter, No. 322, with a glass calomel electrode was used for the titrations.

From the titration curves the average number of proton associated with ANSA ($\bar{n}_A$) was calculated using the relation of Irving-Rossotti :

$$\bar{n}A = Y - \frac{(V''-V').(N^o+E^o)}{(V^o+V').TL}$$

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where, V' and V'' are the volumes of alkali required to reach the same *p*H in the acid and the ligand titrations curves respectively; while V°, TL°, E° and N° are the volume of the mixture, initial concentration of the ligand, initial concentration of the acid and the concentration of titrant respectively. Y is the number of dissociable protons.

From the values of n̄A at various *p*H values proton ligand formation constants, log K_1^H and log K^H were computed by various methods e.g., half integral, point-wise calculation and linear plot methods. The results obtained are recorded in Table 1. The proton-ligand formation curves at various ionic strengths are shown in Fig. 1.

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS, LOG K_1^H, LOG K_2^H OF ANSA AT 35°C AND AT VARIOUS IONIC CONCENTRATIONS

S. No.	Ionic concentration KNO_3 : M	Log K_1^H	log K_2^H	log K_n^H	Method
1.	0.2	8.00	3.40	11.40	a
		7.93	3.35	11.28	b
		8.00	3.40	11.40	c
		8.00	3.40	11.40	
2.	0.1	7.80	3.25	11.05	a
		7.76	3.26	11.96	b
		7.80	3.25	11.05	c
		7.80	3.25	11.05	
3.	0.05	7.50	3.20	10.70	a
		7.40	3.15	10.63	b
		7.50	3.20	10.70	c
		7.50	3.20	10.70	
4.	0	7.20	3.05	10.25	

a. -Half n̄A method
b. -Pointwise Calculation Method
c. -Linear plot Method.

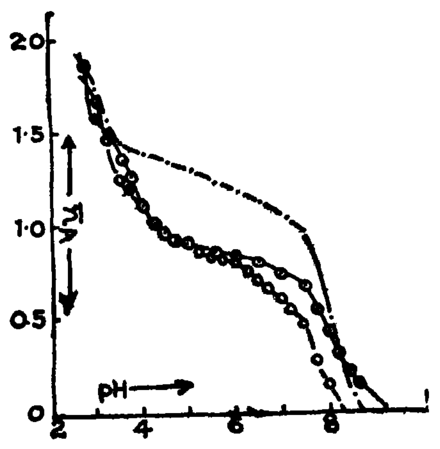
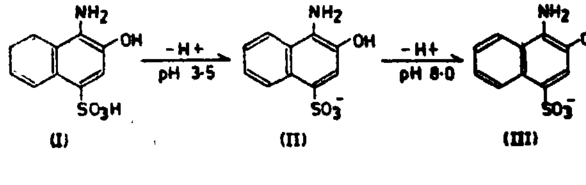
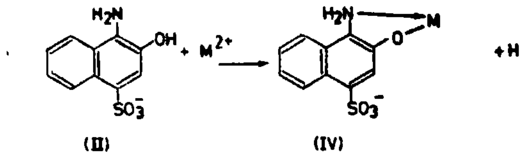


Fig. 1
—.— 0.2 *M*
—⊙— 0.1 *M*
—o—o 0.05*M*

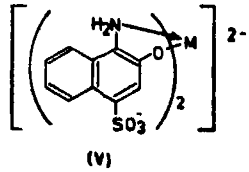
*p*H-titration curve in case of the ligand showed two inflections one at *p*H ~3.5 and the other at *p*H ~8. The first one is associated with the removal of proton from $-SO_3H$ group while the second for the removal of the phenolic hydrogen. Thus the ionisation reaction may be represented as follows:



This indicates that at the physiological *p*H (7.3) the species available for the chelation will be-(II), which will react with trace metals ion of the body with the removal of the phenolic hydrogen in the following manner:



The stoichiometric studies of the chelates formed with the biologically active metals, Mg(II), Ca(II) and Mn(II) and the carcinogenic metals, Fe(III), Al(III), Cr(III), Be(II), Co(II), Ni(II) and Cu(II) were studied using conductometric and potentiometric (*p*H) titrations and applying monovariation method due to Nayar and Pande[6] which indicated formation of two complexes, ML and ML_2, in stepwise manner. Thus the final product with the divalent metal cation may be proposed to have the following structure. This clearly indicates that



most expected coordination number, six for the carcinogenic metal ions is not saturated completely at the physiological *p*H 7.3. This may favour the attachment of the chelates with the tissue and favour cancer formation.

Acknowledgement

One of the authors (Km.) Sarita Shrivastava is thankful to CSIR for award of a Junior Research Fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 673-675

Studies on Some Metal Complexes of 4,6-Dihydroxycoumaran-3-one

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Manuscript received 19 July 1979, accepted 29 December 1979

4,6-Dihydroxycoumaran-3-one gives colour reactions with a number of metal ions on paper chromatograms. Solid complexes of the ligand with V(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zr(IV), Th(IV) and U(VI) transition metal ions were prepared and investigated using infra-red and electronic spectroscopy and thermal and elemental analysis. The results suggest the following formulations for the various complexes. ML_2, where M = VO(II), Cu(II) and Ni(II); $M'L_2.2C_2H_5OH$, where M' = Mn(II), Co(II) and UO_2(II); $M''L_3$, where M'' = Cr(III) and Fe(III); ThL_4. and $ZrL_2.2C_2H_5OH\ Cl_2$.

A number of complexes of β-hydroxy coumaranones are known in literature[1-10], however, no work has been done on the metal complexes of 4,6-dihydroxycoumaran-3-one (Fig. 1). In this ligand the carbonyl is hydrogen bonded to the hydroxyl as shown by its infra-red spectrum $\nu C{=}O$ (1710 cm^{-1}) appears at 1670 cm^{-1} while $\nu O{-}H$ (normal $\sim$3650 cm^{-1}) appears at 3520 cm^{-1}. Further the hydroxyl at position 4 being highly acidic leads to the formation of the anion with relative ease. The compound is thus expected to act as strong chelating ligand.

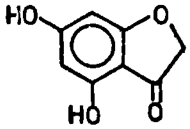


Fig. I

Experimental

4,6-Dihydroxycoumaran-3-one was prepared by Hoesch reaction between phloroglucinol (60g) and chloroacetonitrile in dry ether in the presence of dry HCl and anhydrous $ZnCl_2$ at 0°. The product ω-chlorophloroacetophenone (40g) was refluxed with sodium acetate (60g) for five hours to give 4,6-dihydroxycoumaran-3-one[11]. It is purified by repeated crystallization from water, yield 22g, m p. 254° (lit,[11] 254-255°). The metal complexes were prepared by mixing the metal ion and the ligand in stoichiometric ratio of 1 : 10 (M.L) in ethanol and refluxed on a water bath for one hour. The ligand to metal ratio was kept relatively high to provide for any high coordination number of metal ions. The *p*H range for precipitation was found to be 5.2 to 5.6. The complexes were repeatedly washed with acetone to remove the excess of the ligand. They were recrystallized from alcohol and dried in vacuum over anhydrous calcium chloride.

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The infra-red spectra of the ligand and the complexes were recorded on a Perkin Elmer instrument for the region 4000 to 400 cm^{-1}. Electronic absorption spectra of the complexes was recorded as diffuse refluctance spectra on VSU20 Carl Zeiss spectrophotometer and the elemental analysis for C and H and metal contents were carried out by the usual known methods. The TG curves of the complexes were obtained on the thermobalance (F.C.I., Sindri) and the DTA curves were obtained on DTA-02 Universal apparatus at the heating rate of 10°/min.

Results and Discussion

On the basis of results of elemental analysis for C, H and metal contents (Table 1) the following formulations are proposed for the complex. $[VO(C_8H_5O_4)_2]$; $[Cr(C_8H_5O_4)_3]$; $[Mn(C_8H_5O_4)_2.\ 2C_2H_5OH]$; $[Fe(C_8H_5O_4)_3]$; $[Co(C_8H_5O_4)_2.2C_2H_5OH]$; $[Ni(C_8H_5O_4)_2]$; $[Cu(C_8H_5O_4)_2]$; $[Zr(C_8H_5O_4)_2.\ 2C_2H_5OH]Cl_2$; $[UO_2(C_8H_5O_4)_2.\ 2C_2H_5OH]$ and $[Th(C_8H_5O_4)_4]$.

The infra-red spectrum of the ligand and the complexes (Table 2) support the above formulations proposed for these complexes. The infra-red spectra of the complexes when compared with the corresponding spectrum of the ligand show shifts in principal bands, due to the ν(O−H), ν(C=O) and ν(O−C) stretching modes which occur at 3520, 1670 and 1070 cm^{-1} in the ligand. Table (2) shows that the ν(O—H) stretching mode appears at lower frequencies in the complexes ranging from 3280-3400 cm^{-1}. Similarly the ν(C=O) frequency (1670 cm^{-1}) also gets shifted to much lower values between 1610-1620 cm^{-1}, thereby confirming the coordination of the metal ions through the oxygens of the hydroxyl and the carbonyl group. In addition new bands appear as a result of the ν(M−O) or ν(M—O+C−C) stretching modes. These vibrational

TABLE 1—ELEMENTAL ANALYSIS (%)

S. No.	Complexes	Colour	Calculated C	Calculated H	Calculated M	Found C	Found H	Found M
1.	$VO(C_8H_5O_4)_2$	Yellow	48.36	2.5	12.84	48.0	2.8	13.0
2.	$Cr(C_8H_5O_4)_3$	Red	52.65	2.47	9.58	53.3	3.2	10.0
3.	$Mn(C_8H_5O_4)_2.2C_2H_5OH$	Yellow	50.14	4.5	11.48	50.5	4.0	12.0
4.	$Fe(C_8H_5O_4)_3$	Purple	52.80	2.72	10.13	53.1	2.5	10.6
5.	$Co(C_8H_5O_4)_2.2C_2H_5OH$	Pink	49.80	4.5	12.26	48.9	4.0	12.5
6.	$Ni(C_8H_5O_4)_2$	Pink	49.39	2.5	15.10	49.9	3.1	15.6
7.	$Cu(C_8H_5O_4)_2$	Red	48.79	2.54	16.01	48.3	2.3	10.5
8.	$Zr(C_8H_5O_4).2C_2H_5OHCl_2$*	Pink	41.88	3.76	15.7	42.0	3.5	15.9
9.	$UO_2(C_8H_5O_4)_2.2C_2H_5OH$	Yellow	38.76	2.8	38.5	39.0	3.0	39.0
10.	$Th(C_8H_5O_4)_4$	Brown	43.84	2.24	26.0	45.0	2.5	26.5

*Cl calculated 12.04 ; Found 12.8

TABLE 2—PRINCIPAL BANDS (cm^{-1}) IN THE IR SPECTRA

S. No.	Complex	ν(O-H)	ν(C=O)	ν(O-C)	ν(M—O) or (M—O+C–C)
1.	$C_8H_6O_4$	3520	1670	1070	-
2.	$VO(C_8H_5O_4)_2$	3320	1610	1080	965,530
3.	$Cr(C_8H_5O_4)_3$	3400	1620	1080	500,475
4.	$Mn(C_8H_5O_4)_2.2C_2H_5OH$	3400	1600	1080	450
5.	$Fe(C_8H_5O_4)_3$	3420	1620	1090	430
6.	$Co(C_8H_5O_4)_2 2C_2H_5OH$	3350	1615	1080	450
7.	$Ni(C_8H_5O_4)_2$	3280	1620	1080	440,615
8.	$Cu(C_8H_5O_4)_2$	3400	1600	1080	430
9.	$Zr(C_8H_5O_4)_2.2EtOH.Cl_2$	3400	1600	1080	450
10.	$UO_2(C_8H_5O_4)_2.2EtOH$	3380	1610	1050	1150,825,700
11.	$Th(C_8H_5O_4)_4$	3420	1600	1075	460

modes appear at 965, 330 cm^{-1} in V(IV) 500, 475 cm^{-1} in the Cr(III), 450 cm^{-1} in the Mn (II), 430 cm^{-1} in Fe(III), 450 cm^{-1} in Co(II), 440 and 615 cm^{-1} in Ni (II) 430 cm^{-1} in Cu(II), 450 cm^{-1} in Zr(IV), 1150, 825 and 700 cm^{-1} in U(VI) and 460 cm^{-1} in the Th(IV) complexes. The infra-red spectra of the complexes thus unambiguously confirm the formation of the complexes and the donor sites in the ligand[13-15].

The electronic absorption spectra of the complexes further elucidate the nature and the configuration of the complexes. The bands at 33333, 20000 and 12500 cm^{-1} are assigned to $^2A_1 \leftarrow {}^2B_2$, $^2B_1 \leftarrow {}^2B_2$ and $^2E_2 \leftarrow {}^2B_2$ transitions as is obtained in the square pyramidal complexes of VO^{2+}ion[16]. The octahedral geometry of the Cr(III) complexes is confirmed by the transitions from $^4A_{2g}$ to $^4T_1(P)$, $^4T_{1g}(F)$ and $^4T_{2g}$ arising at 41666, 2871 and 18867 cm^{-1}[7]. The $[Mn(C_8H_5O_4)_2.\ 2C_2H_5OH]$ complex shows bands at 26666, 20000 and 17241 which are assigned to $^4T_{2g}(D) \leftarrow {}^6A_{1g}$, $^4T_{2g} \leftarrow {}^6A_{1g}$ and $^4T_{1g} \leftarrow {}^6A_{1g}$ transition confirming octahedral configuration of the complex. Similarly the octahedral Fe(III) complex being octahedral shows the transitions from $^6A_{1g}$ to $^4T_{1g}$, ^4E_g, and $^4T_{2g}$ at 31258, 27827 and 19047 cm^{-1} respectively. The $Ni(C_8H_5O_4)_2$ complex is assigned a square planar geometry because no transition is found below 10000 cm^{-1} and the bands at 18181, 25000 and 28571 cm^{-1} are assigned to ν_1, ν_2 and ν_3 transitions in the square planar field $Cu(C_8H_5O_4)_2$ has band at 18181 cm^{-1}, indicative of the distorted square planar nature of the complex.

The Zr(IV) complex $[Zr(C_8H_5O_4)_2.\ 2C_2H_5OH]\ Cl_2$ has bands at 43487, 31746, 25000 and 19238 cm^{-1}. These bands are assigned to charge transfer transitions on account of electronic transitions within the ligand, metal ligand and ligand to metal electron transferences[20,21]. The information conveyed by electronic absorption spectra is of limited scope in this case.

The Uranium(VI) complex $[UO_2(C_8H_5O_4)_2.2C_2H_5$-OH]and Th(IV) complex $Th(C_8H_5O_4)_4$ show bands at 40816, 25000 and 20000, 43478, 29411 and 19847 cm^{-1} respectively ; U(VI) and Th(IV) with $5f^0$ electronic configuration have no $5f \rightarrow 5f$ or $5f \rightarrow 6d$ transitions[22]. The appearance of bands in their electronic spectra can obviously be assigned to electron transfer bands.

The chemical composition and the structures proposed on the basis of infra-red, electronic and elemental analysis are further supported by thermal analysis of the complexes (Table 3). The TG curves of Mn(II), Co (II), Zr(IV) and UO_2(II) complexes show two distinct steps due to the progressive loss of two ethanol molecules. The percent loss in mass is in conformily with the suggested decompositions. The DTA in all these complexes show a single endotherm in the region of the loss of two ethanol molecules. The TG curves of Fe(III), Cr(III), V(IV), Cu(II), Ni(II) and Th(IV) complexes do not show any change in the weight loss upto 120°, suggestive of the absence of any coordinated ethanol molecules in them. The decomposition at higher temperature is

TABLE 3—TGA LOSS IN MASS PERCENT

S. No.	Complex	Calculated 1st step	Calculated IInd step	Calculated Final product	Found 1st step	Found IInd step	Found Final product
1.	$VO(C_8H_5O_4)_2$	-	-	77.90	-	-	76.9
2.	$Cr(C_8H_5O_4)_3$	-	-	72.0	-	-	73.0
3.	$Mr(C_8H_5O_4)_2.2C_2H_5OH$	9.6	19.2	74.4	-	19.0	75.0
4.	$Fe(C_8H_5O_4)_3$	-	-	85.6	-	-	85.0
5.	$Co(C_8H_5O_4)_2C_2H_5OH$	9.4	18.9	84.5	10.0	20.0	85.5
6.	$Ni(C_8H_5O_4)_2$	-	-	81.9	-	-	80.1
7.	$Cu(C_8H_5O_4)_2$	-	-	83.6	-	-	82.2
8.	$Zr(C_8H_5O_4).2C_2H_5OH\ Cl_2$	7.77	15.7	78.2	8.5	16.1	78.9
9.	$UO_2(C_8H_5O_4)_2.2C_2H_5OH$	5.9	11.8	64.2	-	12.2	65.0
10.	$Th(C_8H_5O_4)_4$	-	-	70.4	-	-	72.0

continuous and a single broad endotherm is obtaind. No intermediates could be isolated and characterized because of their unstable nature. The final products in all the cases are the corresponding metal oxides i.e., VO_2, CrO_3, MnO, Fe_2O_3, CoO, NiO, CuO, ZrO_2, ThO_2 and U_3O_8. This is confirmed by the calculated weights of these oxides.

From the foregoing discussion it is clear that the infra-red and electronic spectral and thermal analysis studies support the formulations for the complexes. The following tentative structures for these complexes are proposed (Fig 2).

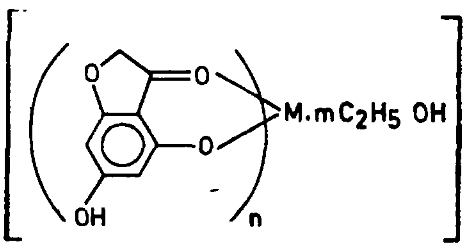


Fig. 2

Where M = Fe(III), Cr(III) ; n = 3 and m = 0
M = Ni(II), Cu(II), Vo(II) ; n = 2 and m = 0
M = Mn(II), Co(II), Zr(IV), UO_2(VI) ;
n = 2 and m = 2
and M = Th(IV) : n = 4 and m = 0.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 676-677

Palladium(II) Chelates of ∝-Oximinoacetoacetarylamide Salicylhydrazones

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Manuscript received 13 May 1979, revised 11 December 1979, accepted 18 March 1980

A number of palladium(II) chelates of the type $Pd(OAASH)_2$ where, OAASH represents salicylhydrazones of ∝-oximinoaceto acetanilide, *o*-toluidide, *p*-toluidide, *o*-chloroanilide, *m*-chloroanilide, *p*-chloroanilide, *o*-anisidide, *p*-anisidide, (2,4)-xylidide, (2,4)-dimethoxyanilide and *p*-phenitidide have been studied. All the chelates are diamagnetic and their infrared spectra suggest the coordination of these ligands through nitrogens of the oximino and salicyl hydrazide moieties. The square planar stereochemistry around the Pd(II) ion in the chelates have been proposed.

IN continuation of our previous work[1-6], the present paper describes the preparation and characterisation of Pd(II) chelates of ∝-oximinoacetoacetarylamide salicylhydrazones.

Experimental

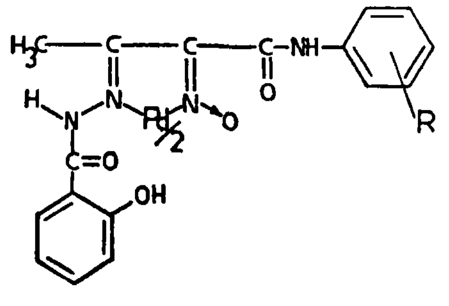
Preparation of the Pd(II) chelate of ∝-oximinoacetoacetanilide salicylhydrazone :

10 ml aqueous solution of Pd(II) chloride (0.05*M*) was gradually added to 25 ml alcoholic solution (2%) of ∝-oximinoacetoacetanilide salicylhydrazone and acidified with dil. HCl. The mixture was diluted to about 100 ml with distilled water and digested on water bath for half an hour, the bright yellow precipitates obtained were filtered, washed with hot water and aqueous ethanol (1 : 1), and dried in an oven at 110°.

The Pd(II) chelates of the other ∝-oximinoacetoacetarylamide salicylhydrazones of the series were prepared in the similar manner. The m.p., colour, elemental analysis and composition of the chelates are given in Table 1.

The infra-red spectra of the ligands and their Pd(II) chelates in KBr pellets and magnetic measurements of the Pd(II) chelates were recorded.

TABLE 1— PALLADIUM CHELATES OF ∝-OXIMINOACETACET-ARYLAMIDE SALICYLHDYRAZONES



No.	R	Composition	Colour	m.p.°C (decomp.)	% Palladium Found	% Palladium Reqd.	% Nitrogen Found	% Nitrogen Reqd.
1.	H	$C_{34}H_{30}N_8O_8Pd$	Bright Yellow	307	13.45	13.60	14.16	14.27
2.	*o*-CH_3	$C_{36}H_{34}N_8O_8Pd$	,, ,,	303	13.13	13.12	13.92	13.78
3.	*p*-CH_3	$C_{36}H_{34}N_8O_8Pd$	,, ,,	310	13.05	13.12	13.72	13.78
4.	*o*-Cl	$C_{34}H_{28}N_8O_8Cl_2Pd$	,, ,,	312	12.45	12.50	13.30	13.12
5.	*m*-Cl	$C_{34}H_{28}N_8O_8Cl_2Pd$	,, ,,	305	12.41	12.50	13.24	13.12
6.	*p*-Cl	$C_{34}H_{28}N_8O_8Cl_2Pd$	Golden Yellow	314	12.43	12.50	13.04	13.12
7.	*o*-OCH_3	$C_{36}H_{34}N_8O_{10}Pd$	,, ,,	295	12.54	12.63	13.40	13.26
8.	*p*-OCH_3	$C_{36}H_{34}N_8O_{10}Pd$	Red	312	12.58	12.63	13.18	13.26
9.	*m*-2,4-$(CH_3)_2$	$C_{38}H_{38}N_8O_8Pd$	Golden Yellow	308	12.61	12.70	13.38	13.32
10.	2,4-$(OCH_3)_2$	$C_{38}H_{38}N_8O_{12}Pd$	Red	303	11.61	11.67	12.35	12.25
11.	*p*-OC_2H_5	$C_{38}H_{38}N_8O_{10}Pd$	Red	296	12.15	12.22	12.95	12.85

*For Correspondence.

Results and Discussion

Magnetic Susceptibility : All the Pd(II) chelates were found to be diamagnetic. Hence the square planar structure for the chelates has been suggested.

Infrared Spectra : The assignment of important infrared bands in free ligands and in their chelates are given in the Table 2. The band at 2600-2632 cm^{-1} appears in the ligands but does not appear in the corresponding chelates which suggests the presence of intramolecular H-bond in the ligands[7]. The absence of this band in the chelates is the indication of the replacement of hydrogen of oximino group by metal ion. The strong band at 965—973 cm^{-1} in the ligands is attributed to N-O stretch. In the chelates this band shifts to 1130-1142 cm^{-1} which suggests the coordination through nitrogen of oximino group[8-11]. The strong band around 1538-1563 cm^{-1} in the ligands belongs to C=N stretching frequency. In the chelates this band appears around 1524-1558 cm^{-1}. The lowering of the C=N stretching frequency is indicating the coordination through 1-nitrogen of salicylhydrazide moiety. The N-N band around 1036-1047 cm^{-1} in the ligands shifts to the higher frequency in the chelates. The magnitude of this positive shift (30-37 cm^{-1}) shows the monodentate linkage of N-N residue as a shift 50 cm^{-1} is usually observed in case of bidentate linking of N-N[12]. The infrared spectra of the ligands and chelates reveal bands around 3300, 3100 and 3500 cm^{-1} indicating secondary trans association and free N-H vibrations of amides respectively[18]. From the Table 2 it is evident that ligands as well as chelates in the solid state are mostly in the associated form. The probable associations are due to H-bonding between carbonyl group and hydrogens of an amide and salicylhydrazide moieties. The strong band around 3300 cm^{-1} is considered to be due to trans associated form. The strong bands in the ligands and chelates around 1620 and 1680 cm^{-1}, 1540 cm^{-1} and 1310 and 1235 cm^{-1} are attributed to amide I, amide II and amide III bands, as associated and free forms respectively[18].

TABLE 2— IMPORTANT INFRARED BANDS OF LIGANDS AND THEIR PD(II) CHELATES (cm^{-1})

No.	$\nu_{C=N}$	ν_{N-O}	ν_{O-H}	ν_{N-H}-(Secondary) Associated		ν_{N-N}
1	1560 s	965 s	2611 mb	3311 s,	3096 s	1036 m
1A	1550 s	1138 s	-	3289 s,	3125 s	1072 s
2	1563 s	966 s	2632 mb	3300 s,	3106 sb	1042 m
2A	1550 s	1130 s	-	3333 b,	3115 m	1072 s
3	1558 sb	966 s	2625 mb	3300 s,	3067 sb	1038 m
3A	1548 sb	1134 s	-	3322 w,	3106 m	1075 m
4	1563 sb	970 s	2632 mb	3311 s,	3086 sb	1040 sm
4A	1548 sb	1136 s	-	3311 w,	3125 m	1075
5	1563 sb	973 s	2632 mb	3300 s,	3067 s	1040 s
5A	1550 sb	1136 s	-	3300 m,	3106 m	1072
6	1563 sb	970 s	2618 mb	3300 s,	3077 s	1040 m
6A	1550 sb	1134 s	-	3279 m,	3125 m	1073 s
7	1563 sb	970 s	2611 mb	3300 s,	3067 s	1040 m
7A	1550 sb	1130 ms	-	3300 m,	3067 m	1075 s
8	1563 sb	970 s	2600 mb	3300 s,	3049 s	1038 m
8A	1558 sb	1136 s	-	3311 w,	3125 m	1073 s
9	1563 s	970 s	2632 mb	3268 s,	3076 s	1047 s
9A	1555 s	1142 s	-	3333 m,	3145 m	1078 s
10	1538 s	970 s	2618 mb	3300 s,	3077 s	1036 s
10A	1524 sb	1136 s	-	3300 m,	3106 m	1070 m
11	1563 s	970 s	2620 mb	3322 s,	3030 m	1040 w
11A	1550 s	1136 s	-	3311 m,	3125 b	1070 m

s=strong, m=medium, w=weak, b=broad, v=very
Serial numbers are according to Table 1 ; numbers without letter A are the ligands and with letter A are the corresponding chelates.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 678-681

Studies on Tin(IV) Complexes of Some Monohydroxamic Acids

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Manuscript received 29 October 1979, accepted 22 December 1979

A number of hexacoordinated dichloro *bis*(hydroxamato) tin(IV) complexes of the general formula R_2SnCl_2 have been prepared from $SnCl_4$ and hydroxamic acids, RH, where RH = R'CONR"OH with R' = C_6H_5, 2-(OH)-C_6H_4, 2-I-C_6H_4, 3, 5-$(NO_2)_2$-C_6H_3 and R" = H, C_6H_5, 2-CH_3-C_6H_4, 3-CH_3-C_6H_4, 4-CH_3-C_6H_4, 4-Cl-C_6H_4. Several physical measurements such as thermogravimetric analysis, conductance, electronic, ir, PMR and mass spectra have been carried out and the results are discussed in terms of structure and bonding of the complexes. The complexes have been found to be octahedral with two chlorine atoms *cis* to each other and the hydroxamate ions acting as bidentate ligands.

HYDROXAMIC acids are weak organic acids[1] with a wide variety of applications including use as commercial floatation reagents in extraction metallurgy, inhibitors for copper corrosion, antifungal agents, pharmaceuticals, food additives, and in nuclear fuel processing. One of the characteristics of hydroxamic acids is their ability to form stable complexes with many metals which forms the basis for their usefulness as analytical reagents[2]. Many metal complexes of synthetic monohydroxamic acids, especially those of iron(III), are also potentially biologically active[3,4]. We have been interested in both the analytical chemistry[5,6] and complex chemistry metals, especially with both inorganic and organic tin, and have made a preliminary report[7]. In the present paper, we wish to report a detailed investigation on the tin(IV) chloride complexes of benzohydroxamic acid (BHA*H*), 2-hydroxybenzohydroxamic acid [2-(OH) BHA*H*], N-phenylbenzohydroxamic acid (PBHA*H*), N-2-methylphenylbenzohydroxamic acid (2-MePBHA*H*), N-3-methylphenylbenzohydroxamic acid (3-MePBHA*H*), N-4-methylphenylbenzohydroxamic acid (4-MePBHA*H*), N-4-chlorophenylbenzohydroxamic acid (4-ClPBHA*H*), N-phenyl-2-iodobenzo hydroxamic acid (P-2-IBHA*H*) and N-phenyl-3, 5-dinitrobenzohydroxamic acid [P-3, 5-$(NO_2)_2$BHA*H*].

Experimental

Reagents and Chemicals :

The hydroxamic acids have been prepared by methods available in the literature[2]. All solvents and chemicals were of reagent grade quality. Benzene was dried by refluxing over freshly cut sodium metal for 48 hr. Methanol was dried by refluxing over magnesium turnings for 48 hr, nitromethane was dried over anhydrous $CaCl_2$ for 72 hr, and all solvents were distilled prior to use.

Preparation of R_2SnCl_2 Complexes :

The tin(IV) hydroxamato complexes, R_2SnCl_2(RH = hydroxamic acid), were prepared by adding a 1-2% ethanolic solution of the required hydroxamic acid (2.5-3.0 molar ratio) to an ice-cold solution of $SnCl_4$ or $SnCl_2$ (containing *ca.* 0.1-0.5 g Sn) in a volume of 200 ml containing 4-6% conc. HCl, when the compounds were precipitated. After allowing to stand for one-half hr, the compounds were filtered, washed with ice-cold water and air dried; they were then recrystallized from a water acetone mixture except $(BHA)_2SnCl_2$ and $[2\text{-(OH)BHA}]_2SnCl_2$. The latter two were recrystallized from a water-ethanol mixture containing few drops of conc. HCl, because of their high solubility in acetone. The recrystallized products were dried in vacuum. The yields were essentially quantitative and all compounds were white crystalline substances except the $[P\text{-}3,5\text{-}(NO_2)_2BHA]_2SnCl_2$ which was slightly brownish. The analytical data and the melting points are given in Table 1. Tin was determined by decomposition of the compounds with conc. HNO_3 and then igniting to SnO_2 and chlorine was determined as silver chloride. Nitrogen was determined by the Jadavpur University Microanalytical Service.

Physical Measurements :

A Chevenard-Joumier Thermobalance (ADAMEL) was used for thermogravimetric analyses. A Phillips conductivity measuring bridge PR-9500 was used for the measurements of conductivities. Electronic spectra were taken with a Hilger Uvispek spectrophotometer using quartz cells. Infrared spectra were recorded as Nujol mulls on KBr discs and on polyethylene plates or as KBr pellets, using a Perkin-Elmer 621, Beckman IR-12 and Perkin-Elmer 337 infrared spectrometers. A Beckman IR-11 spectrometer was used for recording the far infrared spectra. All

TABLE 1—ELEMENTAL ANALYSIS AND PHYSICAL DATA OF THE TIN(IV) COMPLEXES

S. No.	Compound	M.P.(°C)	Elemental Analysis Found/ Calcd. % Sn	N	Cl	Decomposition Temp. Range (°C)	Molar Conductance ($ohm^{-1}cm^2 mole^{-1}$) in Methanol
1.	$(BHA)_2SnCl_2$	260 (dec.)	25.52 25.71	6.10 6.07	15.43 15.36	260-526	195
2.	$[2\text{-}(OH)BHA]_2SnCl_2$	250 (dec.)	23.99 24.05	5.75 5.68	14.46 14.36	250-530	193
3.	$(PBHA)_2SnCl_2$	217	19.24 19.34	4.61 4.56	11.63 11.55	293-576	384
4.	$(2\text{-}MePBHA)_2SnCl_2$	227	18.55 18.49	4.47 4.36	11.12 11.05	288-562	360
5.	$(3\text{-}MePBHA)_2SnCl_2$	203	18.51 18.49	4.41 4.36	11.21 11.05	297-530	388
6.	$(4\text{-}MePBHA)_2SnCl_2$	208	18.43 18.49	4.39 4.36	11.15 11.05	264-528	372
7.	$(4\text{-}ClPBHA)_2SnCl_2$	220	17.27 17.42	4.02 4.01	20.91 20.80	300-590	388
8.	$(P\text{-}2\text{-}IBHA)_2SnCl_2$	200	13.77 13.72	3.16 3.24	-	298-567	392
9.	$[P\text{-}3,5\text{-}(NO_2)_2BHA]_2SnCl_2$	219	14.91 14.96	10.30 10.59	9.01 8.93	289-600	376

ɔectra were calibrated using a polystyrene film with ·espect to the 1601 or 1028 cm^{-1} band (except those aken with Beckman IR-11). PMR spectra were ·ecorded using Varian T-60 and Varian A60A NMR ;pectrometers. Deuterochloroform (99.8%D) and ieuteroacetone (99.7%D) were used as solvents and .etramethylsilane was used as internal stnadard for :aking the PMR spectra. Mass spectra were obtaiıed using AEI MS-902 mass spectrometer at 70 eV.

Results and Discussion

Thermogravimetric Studies :

The thermogravimetric analysis was initially ındertaken in order to investigate whether he complexes obtained from tin(II) .nd tin(IV) chlorides prepared under the ame conditions were the same, and it was found hat the complexes obtained from both tin(II) and .in(IV) chlorides were the same from a study of .heir thermal behaviors The decomposition temɔeratures of tin complexes as obtained from the hermogravimetric curves are given in Table 1. In :ach case the temperatures were raised to 700° and ıll are converted to SnO_2. The complexes decomɔose in such a way that no intermediates are formed during decomposition.

Conductance Studies :

Conductance studies of the complexes have ɔeen made in nitromethane and methanol. All the complexes are found to be non-·lectrolytes in nitromethane having λ_0 values of .9-3.2 ohm^{-1} cm^2mole^{-1} for 1×10^{-3} molar solutions ; the molar conductance values at infinite dilu-ion (λ_0) in methanol are collected in Table 1. In the case of methanol as solvent, the molar conductances (λ_0) have been calculated from the resistanɔes corresponding to different concentrations of the complexes and were then plotted against the $\sqrt{c}$ (where c=concentration) and finally extrapolated to zero concentration to find the molar conductances at infinite dilution, λ_0 . The λ_0 values of the complexes R_2SnCl_2 (RH=ligand) obtained were between 360 and 392 ohm^{-1} cm^2 $mole^{-1}$, except for the complexes $(BHA)_2SnCl_2$ and $[2\text{-}(OH)BHA]_2SnCl_2$. For the latter two complexes the λ_0 values obtained by the above procedure are 195 and 193 $ohm^{-1}cm^2$ $mole^{-1}$, respectively. Since the complexes were found to be non-electrolytes in nitromethane and electrolytes in methanol, the results might be explained by assuming solvolysis of the complexes in methanol. Two kinds of solvolysis may take place as shown in eqs. (1a-1b) and (2a-2b).

$$[R_2SnCl_2]+CH_3OH \rightleftharpoons [R_2Sn(CH_3OH)]^+ + Cl^- \quad \text{... (1a)}$$

$$[R_2SnCl_2)+2CH_3OH \rightleftharpoons [R_2Sn^{2+}(CH_3OH)_2]^{2+} + 2Cl^- \quad \text{... (1b)}$$

$$[R_2SnCl_2]+CH_3OH \rightleftharpoons [R_2Sn(OCH_3)Cl] + HCl \quad \text{... (2a)}$$

$$[R_2SnCl_2]+2CH_3OH \rightleftharpoons [R_2Sn(OCH_3)_2] + 2HCl \quad \text{... (2b)}$$

The λ_0 values in methanol for 1 : 1 electrolytes of the type as shown in eq. (1a) fall in the range 80-115 $ohm^{-1}cm^2mole^{-1}$, and for 2 : 1 electrolytes as shown in eq. (1b) fall in the range 160-220 ohm^{-1} cm^2mole^{-1}[18]. On the other hand, the equivalent conductance values of H^+ and Cl^- ions at infinite dilution in methanol are 141.8 and 51.3 $ohm^{-1}cm^2$ $mole^{-1}$; thus, the calculated λ_0 value for HCl in methanol is 193.1 ohm^{-1} cm^2 $mole^{-1}$[19]. If the solvolysis had taken place according to eq (2b), the conductance value for 2HCl would be $2\times193.1=$ 386.2 ohm^{-1} cm^2 $mole^{-1}$, and the values obtained for all complexes (except $(BHA)_2SnCl_2$ and $[2\text{-}(OH)BHA]_2SnCl_2$) are in the range 360 to 392 $ohm^{-1}cm^2$ $mole^{-1}$, which is reasonably close to the calculated

value from equivalent conductances. The λ_0 values of $(BHA)_2SnCl_2$ and $[2\text{-}(OH)BHA]_2SnCl_2$ are approximately equal to the λ_0 value of HCl in methanol; this value is also comparable to the λ_0 value of the 2 : 1 electrolytes according to eq. (1b). But the latter assumption may be discarded by considering that the solutions of all the complexes in methanol-water mixtures were found to be acidic. It may, therefore, be concluded that the complexes $(BHA)_2SnCl_2$ and $[2\text{-}(OH)BHA]_2SnCl_2$ undergo solvolysis in methanol according to eq. (2a), and all others undergo solvolysis according to eq. (2b). At first sight, this behavior seems surprising, but may not be unreasonable since the ligands BHA*H* and 2-(OH)BHA*H* are somewhat different and their complexes may behave differently, which was also noticed in the mass spectral studies (*vide infra*).

Electronic Spectra :

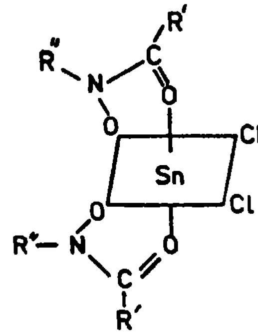
The electronic spectra of all ligands and their tin(IV) hydroxamato complexes, R_2SnCl_2, except the ligands BHA*H* and 2-(OH)BHA*H* and their complexes, have been measured in benzene against a solvent blank in the range 280 to 600 nm. The latter two ligands and their complexes were too insoluble for such measurements. Absorptions in the range 280 to 350 nm were negligibly small for both the ligands and their corresponding complexes. Our results are in conformity with those reported for $Sn(acac)_2X_2$[10] and Sn(IV) complexes with polydentate N,O-ligands[11].

Infrared Spectra :

The infrared spectra in the range 4000 to 70 cm^{-1} for the complexes have been measured along with those of the ligands. A notable feature of the infrared spectra of the complexes is the absence of the ligand stretching modes for both "free" and hydrogen bonded O-H in the ranges of 3030 to 3240 cm^{-1} and 2740 to 2900 cm^{-1}, indicating the replacement of the O-H hydrogen by the metal. The ν(N-H) modes of both $(BHA)_2SnCl_2$ and $[2\text{-}(OH)BHA]_2SnCl_2$ were found at 3280 and 3270 cm^{-1} respectively ; these values remain almost unaffected compared to those of the ligands.

Another distinctive feature of the spectra is the shifting of the C=O stretching frequencies in the complexes from those observed in the ligands. The ν(C=O) mode in the ligands is shifted to 1615-1595 cm^{-1}, owing to hydrogen bonding with N-OH of the ligands. The ν(C=O) values of both ligands and their corresponding metal complexes, along with the shifts, are given in Table 2. In the complexes the carbonyl frequencies lie in the region 1531-1508 cm^{-1}, shifted 70-100 cm^{-1} to lower energy, indicating C=O coordination. Similar results have been observed with the acetylacetonates[12] or other β-diketonates[13]. Another important feature of the spectra was the appearance of new bands due to ν(Sn-Cl) and ν(Sn-O) modes of vibrations in the lower frequency range. The ν(Sn-Cl) mode is reported to occur over the wide region of 365-285 cm^{-1} [10,11,13-15], and we have found a group of new bands of medium to strong intensity in the region 347-315 cm^{-1} (Table 2). The stretching frequencies of Sn-O bonds in the pyridine N-oxide complexes of organic and inorganic tin(IV) appear in the region 400-300 cm^{-1} [16] and in DMSO complexes of tin(IV), the Sn-O vibrations are assigned to 500-400 cm^{-1} bands[17]. In various acetylacetonates of tin(IV) this mode is assigned to 461-404 cm^{-1} bands[18], and in $SnCl_2(CHCl_2CO_2)_2$, the 410 cm^{-1} band is assigned to Sn-O vibration[19]. We have found consistently a band of medium to strong intensity in each of the complexes in the region 455-400 cm^{-1} (Table 2), which may be assigned to Sn-O vibrations.

For all these complexes, two ν(Sn-Cl) vibrations are observed for each complex ; since there are two bands due to ν(Sn-Cl) mode, all the complexes studied must be octahedral with two Cl atoms *cis* to each other, as shown below.



R′ = C_6H_5, 2-(OH),C_6H_4, 2-1-C_6H_4, 3, 5—$(NO_2)^2$—C_6H_3.-
R″ = H, C_6H_5, 2—Me C_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-ClC_6H_4.

PMR Spectra :

The proton magnetic resonance spectra of the R_2SnCl_2 complexes do not differ much from those of the corresponding ligands except that the signals due to NOH protons which were found to occur in the regions $\delta = 9.03$ to 10.40 ppm were lacking. The methyl group signals are all singlets and the aromatic proton signals are complex, and both are observed in the same positions in their corresponding ligands. No 119, 117 Sn...^{1}H couplings were found in the spectra.

TABLE 2—VARIOUS GROUP FREQUENCIES (cm^{-1})

S. No.	Compound	ν(C=O)[a] in Compounds	ν(C=O)[a] in ligands	$\Delta\nu$(C=O)[b]	ν(Sn-Cl)[a]		ν(Sn-O)[a]
1.	$(BHA)_2SnCl_2$	1508 s	1600 s	-92	323 s	315 s	425 s
2.	$[2\text{-}(OH)BHA]_2SnCl_2$	1508 s	1590 s	-82	329 msh	322 m	400 m
3.	$(PBHA)_2SnCl_2$	1515 s	1615 s	-100	332 s	325 s	438 s
4.	$(2\text{-}MePBHA)_2SnCl_2$	1528 s	1600 s	-72	344 s	332 s	450 s
5.	$(3\text{-}MePBHA)_2SnCl_2$	1525 s	1595 s	-70	347 s	330 s	455 m
6.	$(4\text{-}MePBHA)_2SnCl_2$	1530 s	1600 s	-70	332 s	325 ssh	420 m
7.	$(4\text{-}ClPBHA)_2SnCl_2$	1521 s	1592 s	-71	344 msh	335 s	430 m
8.	$(P\text{-}2\text{-}IBHA)_2SnCl_2$	1530 s	1615 s	-85	347 ssh	338 s	421 s
9.	$[P\text{-}3,5\text{-}(NO_2BHA]_2SnCl_2$	1531 s	1615 s	-84	340 msh	331 s	421 m

[a] s = strong, sh = shoulder, m = medium. [b] Minus sign indicates shifts towards lower frequencies.

Mass Spectral Study :

The mass spectra of six tin(IV) hydroxamato complexes, namely $(BHA)_2SnCl_2$, $(PBHA)_2SnCl_2$, $(2\text{-}MePBHA)_2SnCl_2$, $(3\text{-}MePBHA)_2SnCl_2$, $(4\text{-}MePBHA)_2SnCl_2$, $(4\text{-}ClPBHA)_2SnCl_2$, were recorded at a probe temperature of 230° using 70 eV electrons. All the spectra were characterized by polyisotopic "clusters" at different m/e ratios, especially at the high m/e values. The mass spectra of all the complexes [except $(BHA)_2SnCl_2$] show the molecular ions as the highest peaks, and the molecular weights obtained from the mass spectral data were the same as the formula weights. In the case of $(BHA)_2SnCl_2$ no peaks higher than m/e = 260 have been observed, whereas the formula weight is 462. The peak at m/e = 260 for $(BHA)_2SnCl_2$ may be assigned to $ClSnOC_7H_5^+$ ion. The results indicate that the five complexes $(PBHA)_2SnCl_2$, $(2\text{-}MePBHA)_2SnCl_2$ $(3\text{-}MePBHA)_2SnCl_2$, $(4\text{-}MePBHA)_2SnCl_2$ and $(4\text{-}ClPBHA)_2SnCl_2$ are somewhat more stable than the $(BHA)_2SnCl_2$ complex under the conditions of the experiments. The fragmentation patterns follow a regular trend reflecting successive loss of chlorine atoms, methyl groups (where they are present) and even loss of a ligand. In some cases, it was found that $C_6H_5CO^+$, $C_6H_5N^+$, $CH_3C_6H_4N^+$ or $ClC_6H_4N^+$ ions are lost, leading to complete decomposition to Sn^+. In addition, in some cases a rearrangement leading to the formation of $SnC_6H_5^+$ ion had taken place. The spectral features of $(2\text{-}MePBHA)_2SnCl_2$, $(3\text{-}MePBHA)_2SnCl_2$ and $(4\text{-}MePBHA)_2SnCl_2$ are very similar, whereas the spectra of the $(PBHA)_2SnCl_2$ and $(4\text{-}ClPBHA)_2SnCl_2$ are somewhat different from these. The spectral characteristics of $(BHA)_2SnCl_2$ is significantly different from all the others ; first, it does not have any molecular ion peak, and second, the decomposition route which could be deduced from the spectra was different, since the ligand itself is somewhat different. The complex also melted with decomposition whereas the others did not.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 682-684

Reactions of Aminoalkanols with Some Ni(II) Complexes of the Mixed and *Bis* (Schiff Base) Ligands

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Manuscript received 10 October 1979, accepted 30 December 1979

Reactions of aminoalkanols have been carried out with mixed and *bis* (Schiff base) complexes of nickel(II). In these reactions both the ligands combine with the aminoalkanol forming tridentate ligand, here -H of the -OH group is not removed. Therefore, both the ligands are retained and they behave as bidentate ligands. From the resulting nickel(II) complexes the tendency to form the Schiff base in the coordinated ligand is found to be similar for salicylideneamine, 2-hydroxy-1-naphthyl methyleneamine and 1-(2-hydroxy phenyl) ethylideneamine. The complexes formed have been characterized by analytical, spectral and magnetic studies.

A good number of examples of complexes formed by potential tridentate Schiff base ligands have been summerized by Goodwine[1,2]. The Schiff base, N-hydroxy ethylsalicylideneamine was found to act as a tridentate ligand with nickel (II)[3] and titanium (IV)[4] ions. This tridentate Schiff base ligand form 1 : 2 complexes with nickel(II), the alcoholic hydroxyl group of the ligand was presumed to coordinate through its oxygen atom, but the $-OH$ proton remained undissociated[3,5]. This fact suggests that tridentate Schiff bases have a great tendency to form stable nickel (II) complexes having 1 : 2 composition. An attempt was, therefore made to study the reactions of aminoalkanols with *bis* (bidentate Schiff base) complexes of nickel (II), and to confirm the formation of nickel (II) complexes with tridentate Schiff bases through amine exchange reaction. The reactions were also carried out on mixed imine Schiff base complexes of nickel (II) which are reported earlier[6,7]. The structures of the resulting Schiff base complexes have been discussed, and the mechanism of the formation of the 1 : 2 and 1 : 1 : 1 has been suggested in case of *bis* and mixed complexes respectively.

Experimental

All the six complexes used for the reactions with aminoalkanols were prepared according to the published procedures[6-8].

(i) *Reactions with bis [1-(2-hydroxyphenyl) ethylideneamine] Ni(II)* :

A solution of mono ethanol amine (mea) or isopropanol amine (ipa) (3 ml) in 30 ml of ethanol was added to a suspension of (1g) title imine-complex in 50 ml of ethanol. Well stirred reaction mixture was refluxed for 1 hr. and water was added in order to get the solid compound. It was filtered, washed with water and ethanol and air dried.

(ii) *Reactions with the mixed Schiff base complexes of nickel (II)* :

The reactions were carried out with the following mixed compounds :

(a) [Salicylideneamine, 1-(2-hydroxyphenyl) ethylideneamine] Ni(II).

(b) [2-Hydroxy-1-naphthyl methyleneamine, 1-(2-hydroxypnenyl)-ethylideneamine] Ni (II).

A solution of mea or ipa (3 ml) in 30 ml of ethanol was added to a suspension of the complex (a) or (b) (1g) in 50 ml of ethanol.

The reaction mixture was refluxed for 1hr. The reaction mixture was stirred well and water was added to obtain the solid compound. The solid compound obtained in each case was filtered, washed successively with water and ethanol and air dried.

The complexes have been analysed for metal, N, C and H (in some cases). The results are reported in Table 1. Conductivity measurements were carried out in chloroform using a Toshniwal conductivity bridge type CLOI/OIA. The magnetic susceptibilities of the complexes were determined at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. Infrared Spectra of the complexes were recorded in the form of KBr pellets. The electronic spectra of the complexes in chloroform solution were taken on a Beckman DU-2 spectrophotometer at room temperature using 1 cm quartz cells in the range of 400-1000 nm. The reflectance spectra in LiF medium have been obtained for some of the complexes.

*The work is carried out at Chem. Dept., M.S. Univ. of Baroda.

TABLE 1—ANALYTICAL, ELECTRONIC SPECTRAL BAND AND MAGNETIC MOMENT OF *bis* AND MIXED AMINOALKANOL SCHIFF BASE COMPLEXES OF Ni(II)

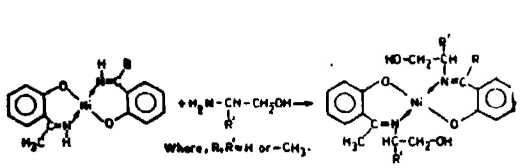
No.	Complex	Found (Calculated) % Ni		C		H		N		λ_{max} (nm)	$\mu_{eff.}$ (B.M.)
1.	*Bis* [N-Hydroxyethyl-1-(2-hydroxy phenyl) ethylideneaminato] Ni(II).	14.15	14.25	-	-	-	-	6.75	6.85	620	3.12
2.	N-Hydroxyethyl [(salicylidene-aminato), (2-hydroxyphenyl)-ethylideneaminato] Ni(II).	14.72	15.14	-	-	-	-	6.98	7.00	650	3.08
3.	N-Hydroxyethyl [(2-hydroxy-1-naphthyl-methyleneaminato), 1-(2-hydroxyphenyl) ethylideneaminato] N(II).	13.02	12.90	61.23	61.02	5.32	5.22	6.21	6.00	750 820	3.03
4.	*Bis* [N-Hydroxy-iso-propyl-1-(2-hydroxyphenyl) ethylideneaminato) Ni(II).	13.26	13.50	-	-	-	-	6.32	6.50	630	3.04
5.	N-Hydroxy-iso-propyl-[salicylideneaminato, 1-(2-hydroxy phenyl) ethylideneaminato] Ni(II).	13.63	13.48	58.53	59.02	6.50	6.15	6.50	6.25	650	3.10
6.	N-Hydroxy-iso-propyl-[2-hydroxy-1-naphthylmethyleneaminato, 1-(2-hydroxyphenyl) ethylideneaminato] Ni(II).	12.26	12.16	-	-	-	-	5.85	5.63	650	3.14

The molar conductance of all the nickel (II) complexes in chloroform show them to be non-electrolytes. The magnetic and spectral data have also been presented in Table 1.

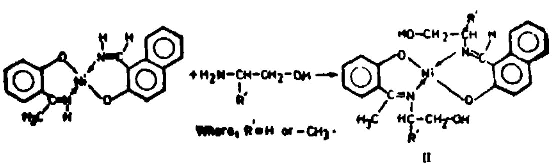
Results and Discussion

The reactions of mea with *bis* and mixed imine complexes gave the amine-exchange products (1), (2) and (3), respectively. Similar reactions take place with ipa and the products obtained are (4), (5) and (6).

In nickel (II) complexes, however, the solid obtained corresponds to the composition [Ni—L_2] or [Ni—L—L'], where L=N-hydroxyethyl or isopropyl-1-(2-hydroxyphenyl) ethylideneamine and L'=N-hydroxyethyl *or isopropyl-salicylideneamine* or 2-hydroxy -1-naphthyl methyleneamine. In *bis* and mixed nickel (II) complexes both the ligand molecules react with mea or ipa to form tridentate ligands. The reaction schemes proposed are as follows :



I



II

Thus it is observed that the Schiff base of aminoalkanols with aldehyde and ketone acts as bidentate ligand and the -OH group of the Schiff base remains uncoordinated. This is because the Schiff base with a double bond cannot occupy two equitorial and two axial positions[9,10]. If the -OH groups would have coordinated, losing the proton, the complex would have been ionic. But it is observed that compounds are insoluble in water and soluble in organic solvents. The conductivities of their solutions show them to be non-electrolytes. Similar structures of *bis* tridentate Schiff base complexes of nickel (II) with non-coordinated -OH groups have been reported earlier[3,6].

The structure can be explained by the analogy with *bis* (N-hydroxy ethyl-salicylideneaminato) Ni(II) complex, prepared by Yamada and coworkers[3] and Poddar *et al*[5] by direct action of the metal salt with N-hydroxy ethyl salicylideneamine. They have found an octahedral configuration of the Ni(II) complexes on the basis of electronic absorption spectra and both in the solid state and in solution and magnetic moment value ($\mu_{eff.}$=2 95 B.M.).

Present *bis* and mixed nickel(II) Schiff base complexes are mastared and green in colour. These complexes show magnetic moment values between 3.1 to 3.28 B.M. This suggests that the complexes have an octahedral configuration. Since, the two ligands are bidentate there should be a tetra coordinated square planar structure. However, the octahedral geometry may be due to partial coordination between metal and oxygen atom of alcoholic -OH group, or it may be due to the polymerization. This situation occurs when the distortion from the square arrangement of the donor atoms with respect to metal atom arises from nonplanarity of the ligand molecules. This nonplanarity of the ligand molecule probably arises from steric interaction[1,11]. The solubility of the compounds in water and other organic solvents is very low indicating that the compounds may be polymeric.

The electronic absorption spectra, both in the solid state and in solutions of Ni(II) *bis* and mixed Schiff base complexes show a broad band between 600 to 650 nm. There is an increase in optical density after 800 nm. This shows that the compounds have an octahedral structure in the solid state.

The ir spectra of 1 : 2 and 1 : 1 : 1 nickel(II) Schiff base complexes shows a broad band in the range 3600-3300 cm^{-1} corresponding to O-H stretching frequency indicating the undissociated hydrogen of OH group. *Bis* and mixed-imine Schiff base complexes of nickel (II) show a band at 3300 cm^{-1} corresponding to -N-H stretching frequency. The disappearance of the 3300 cm^{-1} band after amine exchange reaction can be attributed to the replacement of the N-H hydrogen in nickel *bis* and mixed imine Schiff complexes by an alkanol amine group. The two weak bands observed at 2920 and 2860 cm^{-1} correspond to C–H stretching frequency due to $-CH_2$ group and aldehydic C–H, respectively. In nickel(II) complexes (Structure-I) the C=N stretching band appears at 1650 cm^{-1} while in nickel(II) complexes (Structure II) it appears at 1620 cm^{-1}. All these complexes show a band at 1450 cm^{-1} due to C–H bending. In all the complexes there is a band near 1300 cm^{-1} corresponds to C–O stretching. The band observed at 820 cm^{-1} in all the complexes is due to the O–H bending.

Acknowledgement

I gratefully acknowledge the help and suggestion of Dr. P.K. Bhattacharya, Reader, Department of Chemistry, M.S. University of Baroda in this work.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980 pp. 685-687

Spectrophotometric Studies on Vanadium(V), Niobium(V) and Tantalum(V) Complexes with Violuric Acid

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Manuscript received 16 March 1979, accepted 30 December 1979

Spectrophotometric measurements in the ultraviolet region within the range 200-250 nm is performed to study the reaction of violuric acid with vanadium(V^{5+}), niobium (Nb^{5+}) and tantalum (Ta^{5+}). The results obtained verified that V^{5+}, Nb^{5+}, and Ta^{5+} form chelate compounds with measurable absorbance at λ=208, 212 and 217 nm in buffer solutions of *p*H 9.5, 9 and 9, for $V^{5}\pm$, $Nb^{5}\pm$ and $Ta^{5}\pm$ violurate solutions, respectively. The stoichiometry and the stability constants of the complexes were determined from the spectrophotometric data.

In the present work, the formation of complex compounds between violuric acid and V^{5+}, Nb^{5+} and Ta^{5+} ions as the spectrophotometric measurements indicate, are reported and discussed.

VIOLURIC acid is of great use as a good organic complexing reagent for the formation of metal-chelate compounds and a metal indicator for the an analytical (volumetric and gravimetric) determinatoin of minute amounts of transition metals.

Violuric acid was introduced as an indicator for the complexometric titration of copper with complexon(III)[1]. Violuric acid was also used for the gravimetric microdetermination of palladium[2] and for the photometric determination of copper[3]. Niobium (V) and tantalum (V) were determined spectrophotometrically using oxine[4], alizarin red S and quinizarin -3-sulphonic acid[5].

Experimental

Solutions :

Standard solutions ($5\times10^{-3}M$) of either V^{5+}, Nb^{5+}, or Ta^{5+} were prepared by dissolving the appropriate amount of V_2O_5 (A.R., 99.9%) in hot HCl (A.R.), few mls of HNO_3 (A. R.), then completing the solution to the requisite volume using bidistilled water, and fusing the A.R. Nb_2O_5 and Ta_2O_5 (99.9%) with $K_2S_2O_7$ and dissolving the cake in 20% tartaric acid[6].

$1\times10^{-2}M$-Violuric acid solution was prepared by dissolving the accurately weighed portion of the reagent in redistilled water.

Oxalic, boric, succinic acids, Na_2SO_4, $Na_2B_4O_7.10H_2O$ and Na_2CO_3 buffers of *p*H 1.5-11 were prepared according to Thiel, Schulz and Coch[7] and standardised using Pye Unicam Model 290, 2 *p*H Meter.

Working Procedure :

The spectrophotometric measurements in the ultraviolet region were recorded on the Pye Unicam SP 8000, Ultraviolet Recording Spectrophotometer with matched silica cells, 1 cm light path. The working solution was prepared by mixing the metal ion with ligand-buffer mixture, using blank solution containing the same concentration of violuric acid as in the case of the test solutions of $V^{5}\pm$, $Nb^{5}\pm$ and $Ta^{5}\pm$, violuric acid to compensate the effect of absorbance due to ligand.

Results and Discussion

On mixing V^{5+}, Nb^{5+} or Ta^{5+} solution with violuric acid a pale rosy colour is developed due to the formation of complex compounds.

Spectrophotometric Measurements :

The spectrograms of $V^{5}\pm$, $Nb^{5}\pm$ and $Ta^{5}\pm$ violurate complexes are characterised by one apparent maximum peak. The spectral absorbance of the chelates is affected by some factors which are discussed briefly in the followings :

i) *Effect of pH* ;

$1\times10^{-5}M$ solutions of either V^{5+}, Nb^{5+} or Ta^{5+} and $4\times10^{-5}M$-violuric acid were used for studying the influence of *p*H on the complex formation. The spectral absorbance of the solutions increases with the increase of *p*H reaching maximum at *p*H 9.5 in case of $V^{5}\pm$ violurate (λ_{max} = 222 nm) and 9 in case of $Nb^{5}\pm$ (λ_{max} = 212 nm) and $Ta^{5}\pm$ violurate (λ_{max} = 215 nm) complexes then slows down. At the

same time the absorption bands shift to a higher wavelength as the pH increases. This may be due to the generation or progressive formation of different interconvertible species.

The increase of absorbance may be attributed to the probable and gradual increase of complex formation whereas the decrease of absorbance beyond the maxima may be due to the effect of higher alkalinity of buffer solution which may cause a dissociation (or hydrolysis) to the complexes formed or form another sort of complexes.

ii) *Effect of Violuric Acid Concentration* :

On keeping the metal ion concentration invariable at $5\times10^{-6}M-V^{5+}$, $1\times10^{-4}M-Nb^{5+}$ and $5\times10^{-6}M-Ta^{5+}$, whereas that of violuric acid is chan... from $8\times10^{-7}M-5\times10^{-5}M$ in the case of V^{5+}V A. solutions, $6\times10^{-5}M-6\times10^{-4}M$ in case of Nb^{5+}- V.A. solutions and $1\times10^{-6}M-5\times10^{-5}M$ in case of Ta^{5+}-V.A. solutions, the spectral absorbance increases gradually with the increase of ligand concentration, then tends to approach a limiting value in case of V^{5+} and Ta^{5+} due to saturation attainment. Maximum absorption band does not alter in case of Nb^{5+}, whereas in case of V^{5+}-V.A., λ_{max} shifts to $\lambda = 205$ nm (hypsochromic shift) and λ_{max} in case of Ta^{5+}-V.A. shifts to 204 nm (hypsochromic shift) with the increase of violuric acid concentration.

(iii) *Effect of Metal Ion Concentration* :

On keeping the violuric acid concentration constant at $2\times10^{-5}M$, whereas that of V^{5+} was changed from 5×10^{-6}M to $5\times10^{-7}M$, that of Nb^{5+} was varied from $5\times10^{-6}M$-3×10^{-4} $M$and that of Ta^{5+} was changed from $1\times10^{-6}M$ to $4\times10^{-5}M$, the spectral absorbance of $V^{5}\pm$, $Nb^{5}\pm$ and $Ta^{5}\pm$violurate complexes increases with the increase of metal ion concentrations. λ_{max} shifts to 208 nm in case of $V^{5}\pm$V. A., 218 nm in case of $Nb^{5}\pm$ V. A., and 217 nm in case of $Ta^{5}\pm$V. A. complexes, at higher metal ion concentration, while at lower concentrations, λ_{max} appears at $\lambda = 205$, 228 and 215 nm in case of $V^{5}\pm$ V.A., $Nb^{5}\pm$V.A. and $Ta^{5}\pm$V.A. complexes, respectively.

Beer's law is valid for applying violuric acid as analytical reagent for the microdetermination of the elements. The lowest amounts that can be /detected and determined are 5.1 ppm, 7.4 ppm and 1.8 ppm with extinction modulus 3.6×10^{7}, 2.5×10^{4} and 3.7×10^{5} for V, Nb and Ta (as metals), while the highest amounts are 101.9 ppm, 37.2 ppm and 7.2 ppm having extinction coefficient values equal to 7.9×10^{6}, 2.95×10^{4} and 2.7×10^{6} for V, Nb and Ta (as metals), respectively. The higher values of extinction coefficient make the method easier to be applied for the determination of microamounts of the metals.

Stoichiometry of the complexes :

The stoichiometric ratios of the complexes were determined under optimum conditions favouring maximum colour development. The methods applied for the determination of the stoichiometry (composition) of the chelates are the molar ratio (M.R.), straight line (S.L.), continuous variation (C.V.), slope ratio (S.R.), and limiting logarithmic (L.L.). The results obtained are recorded in Table 1. These results reveal the formation of 2:1, 1:1, 1:2, 1:3 and 1:4 complexes.

TABLE 1—STOICHIOMETRIC COMPOSITION OF $V^{5}\pm$, $Nb^{5}\pm$ AND $Ta^{5}\pm$ VIOLURATE COMPLEXES

Method	$V^{5}\pm$ chelates	$Nb^{5}\pm$ chelates	$Ta^{5}\pm$ chelates
M.R.	2:1, 1:1, 1:2 1:4.	1:1, 1:2, 1:3	2:1, 1:1, 1:2. 1:3
C.V.	2:1, 1:1, 1:2	2:1, 1:1, 1:2 ; 1:3, 1:4	2:1, 1:1, 1:2 1:3, 1:4
S.L.	1:1, 1:2, 1:4	1:1, 1:3, 1:4	1:2, 1:3
S.R.	1:1, 1:2	1:4	1:1
L.L.	1:1, 1:3	1:3	1:4

M.R. = molar ratio, C.V. = continuous variation, S.L. = straight line, S.R. = slope ratio, L.L. = limiting logarithmic.

The Apparent Formation Constant :

The values of the apparent formation (stability) constants of the chelates established in solution were evaluated from the results of the spectrophotometric methods, namely, the molar ratio, continuous variation, straight line and limiting logarithmic methods, are reported in Table 2. The equation

TABLE 2—VALUES OF FORMATION CONSTANTS OF $V^{5}\pm$-, $Nb^{5}\pm$- AND $Ta^{5}\pm$- VIOLURATE COMPLEXES

Method	Ratio	Kf of metal chelate of V^{5+}	Nb^{5+}	Ta^{5+}
M.R.	1:1	3.582×10^{9}	0.197×10^{9}	$3.621\times^{10}$
	1:2	1.942×10^{14}	1.657×10^{14}	2.686×10^{16}
	1:3		4.356×10^{19}	1.2997×10^{34}
	1:4	4.485×10^{27}		
C.V.	1:1	0.275×10^{9}	0.744×10^{9}	0.144×10^{9}
	1:2	5.971×10^{14}	2.314×10^{14}	
	1:3			0.835×10^{21}
	1:4		0.267×10^{26}	
S.L.	1:1	0.748×10^{8}	0.020×10^{9}	
	1:2	9.21×10^{14}		0.255×10^{16}
	1:3		0.803×10^{19}	0.297×10^{23}
	1:4	8.483×10^{29}	0.085×10^{26}	
L.L.	1:1	2.58×10^{8}		
	1:2			
	1:3	1.712×10^{25}	0.347×10^{22}	
	1:4			2.976×10^{33}

utilised for the determination of K_f by molar ratio and continuous variation methods has the form :

$$K_f = \frac{(A/Am)}{[1-(A/Am)]\,(^{n+1}).\,n^{n}[L]^{n}}$$

where :

K_f = apparent fromation constant,

A = absorbance at a given ligand concentration, L,

Am = limiting absorbance,

n = stoichiometric ratio (number of ligand groups in the chelate molecule).

For the straight line method, β_n can be determined from the relation :

$\beta_n = \log ([M^{n+}] . [L]) / (\log A - \log V)$ in which V = volume of the mixed solution.

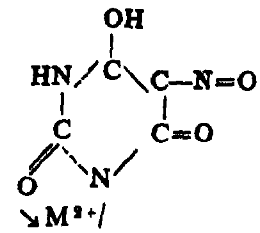
From the results of the limiting logarithmic method, β_n and hence, K_f can be calculated by using the equation :

$$\log \beta_n = \log (A/\epsilon_n) - (m \log [M^{n\pm}] + n \log [L])$$

where :

ϵ_n = molar extinction coefficient of the complex with the stoichiometric ratio (ligand/metal ion) = n.

The chelation between violuric acid and V^{5+} Nb^{5+} and Ta^{5+} can be typified as follows :



(1 : 1)

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 688-689

Extraction of Chromium(VI) from Aqueous Ortho-Phosphoric Acid Solutions by Tri-*n*-Octylphosphine Oxide

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Manuscript received 20 April 1979, revised 7 November 1979, accepted 19 December 1979

The extraction of chromium(VI) from ortho-phosphoric acid solutions by tri-*n*-octylphosphine oxide has been studied. The nature of the extracted species is established.

THE use of phosphorous containing solvents [1-4] and other extracting systems [4-8] for the extraction of chromium(VI) has been reported by several workers and the extracted species are identified as $CrOX^-$ from HX solutions (X=Cl or Br) and as $Cr_2O_7^{2-}$ from other mineral acid systems.

The present communication describes our studies on the extraction of chromium(VI) by tri-*n*-octylphosphine oxide (TOPO) from ortho-phosphoric acid solutions in order to identify the extracted species.

Experimental

Materials: A 0.5*M* stock solution of chromium trioxide (E. Merck) was prepared and standardised with standard Fe^{2+} solution, using *n*-phenylanthranilic acid (NPA) as indicator and diluted asrequired.

TOPO (Eastman Kodak Company, Rochester, N.Y.), a white crystalline solid (Molecular weight 387) was used. 0.2*M* solution of TOPO in cyclohexane was prepared and employed in the studies. All other chemicals used were of reagent grade or purified by standard methods. Phosphorus-32 (carrier free) in the form of ortho-phosphoric acid in HCl was obtained from Isotope Division, B.A.R.C., Bombay.

Equipment: β^- activities of the solutions were measured using a liquid G.M. counting setup (ECIL, Hyderabad). The distribution of chromium (VI) was followed spectrophotometrically using a Unicam model SP600 spectrophotometer. Absorption spectra were taken on a Shimadzu Double beam spectrophotometer model UV-140.

Procedure: Chromium(VI) distribution studies were made using appropriate concentrations of of chromium(VI) and ortho-phosphoric acid by equilibrating for about 3 to 5 minutes with an equal volume (10 ml) of 0.20*M* TOPO in cyclohexane which is preequilibrated with 1*M* ortho-phosphoric acid solution. The amount of chromium(VI) upto 2g/l in the aqueous phase was determined spectrophotometrically by means of diphenyl carbazide[9]. Higher concentrations of chromium(VI) (>2g/l) were determined iodometrically.

The distribution of ortho-phosphoric acid as a function of chromium(VI) concentration was studied at 1.0*M* ortho-phosphoric acid concentration using ^{32}P as tracer using the same procedure. The non-exchange of ^{32}P activity between the aqueous $H_3{}^{32}PO_4$ and phosphorus in TOPO has been established before conducting these studies.

Results and Discussion

Extraction of Chromium (VI) as a Function of Acidity:

In order to find out the effect of acidity on the extraction of chromium(VI), extractions were carried out at various concentrations of ortho-phosphoric acid, using 0.20*M* TOPO in cyclohexane pre-equilibrated with 1*M* H_3PO_4, and 0.001*M* chromic acid. The distribution coefficients gradually increased with increasing acidity and were independent of acidity over the range 0.75*M*-1.5*M* ortho-phosphoric acid followed by a gradual fall upto 3*M*, beyond which chromium(VI) undergoes reduction to chromium(III).

Composition of the Extracted Species:

The composition of the extracted species was determined by the maximum loading experiments and also by the distribution ratio method[10]. The maximum loading of 0.20*M* TOPO with chromium(VI) at 1*M* aqueous acidity yielded a mole ratio of the [extractant] to [chromium (IV)]$_{org}$=unity. A plot of log [TOPO]vs log K_d in the distribution ratio method gave a straight line with a slope of 1.10. The method of least squares has been applied to the points of the plot and the slope of the straight-line was verified by calculation (slope =1.15). These studies show that the solvation

number with TOPO for chromium(VI) species in in 1*M* ortho-phosphoric acid medium is unity.

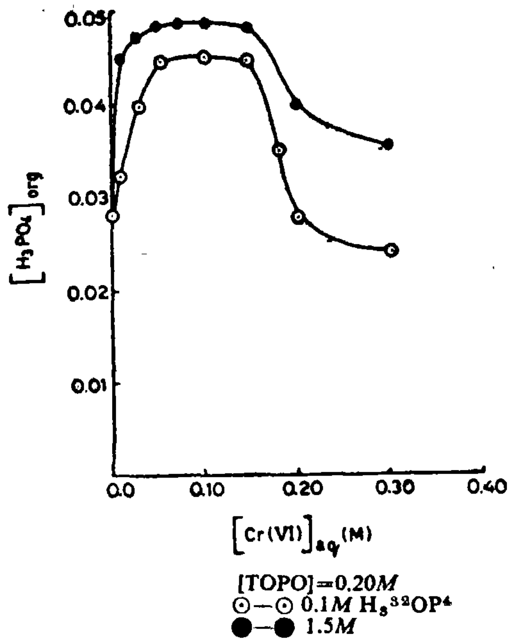


Fig. 1. Distribution of phosphoric-acid as a function of Cr(VI).

In order to find out the association of phosphate with the extracted species, distribution studies were carried out from 1*M* phosphoric acid solutions tagged with ^{32}P tracer varying the aqueous chromium(VI) concentration and using 0.20*M* TOPO pre-equilibrated with 1*M* ortho-phosphoric acid (Fig. 1).It is seen that initially the concentration of ortho-phosphoric acid in the organic phase gradually increased with increasing chromium(VI) concentration, reaching a maximum value and remained constant, over the aqueous chromium(VI) concentration range, 0.05 to 0.15*M* and then gradually decreased. This clearly shows that the extracted chromium(VI) is present as a mixture of species containing predominantly phosphato-chromate.

Absorption Spectra :

The above findings are further confirmed by measurement of absorption spectra of the extracted species. The individual chromium(VI) species can be identified on the basis of their differences in absorption maxima in the U.V. region, [11-13]. The characteristic absorption maxima for $Cr_2O_7^{2-}$ lie at 280 and 355 nm. The absorption spectra of chromium(VI) species extracted at various aqueous acid phase concentrations keeping the aqueous phase chromium(VI) concentration constant, showed absorption maxima at 280 and 355nm, but the molar extinction coefficient at 280nm changed gradually from $\varepsilon=2200$ to $\varepsilon=1900$ with a gradual increase in the concentration of phosphoric acid from 0.1*M* to 15*M*0 and remained constant thereafter.

In aqueous mineral acid systems chromium(VI) exhibits[1,11-13] various equilibria giving rise to different species. The protonation of $HCrO_4^-$ by the mineral acids was suggested by several workers[14-17]. In orthophosphoric acid solutions the species can be represented by the equilibrium,

$$HCrO_4^- + H^+ + H_3PO_4 \rightleftharpoons HOCrO_2 - OPO_3H_2 + (H_3CrPO_7)$$

Under the conditions the extractable species could be H_3CrPO_7, H_2CrO_4 and $H_2Cr_2O_7$. The extractability of the second and the third species with TBP has already been reported[1]. It now appears that at high ortho-phosphoric acid concentrations the first species is formed to a significant extent leading to its extraction with TOPO. Furthur attempts to study the extraction of chromium(VI) in dilute ortho-phosphoric acid solutions with TOPO were not successful as the extractions were partial.

Acknowledgement

One of us (M.V.N.M.) is thankful to the U.G.C., New Delhi, for the award of a Teacher Fellowship under the Faculty Improvement Programme.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 690-692

Synergistic Effect Using Organic Base on Extraction of Co(II) Acetyl Acetonate in Xylene

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Manuscript received 17 April 1979, accepted 29 December 1979

The adducts formed between Co(II) acetyl acetonate and a number of bases have been identified and their formation constants determined by the synergistic effects of the various organic amines on the extractability of the cobalt into xylene. The results show that the synergism is due to the formation and preferential extraction of 1 : 1 or 1 : 2 adducts.

THE mechanism of synergism in the extraction of Co(II) acetyl acetonate is the formation of base adducts in the organic solvent[1-7]. The formation constant $K_{2,n}$ of the base adduct is a quantitative measure of the synergistic enhancement by the neutral base. Further, it is known that water molecules play an important role in the equilibria of the species in the organic phase[8-11].

$$[Co(AcAc)_2 nH_2O]_o + nL = [Co(AcAc)L_n]_o + n(H_2O)$$

where o denotes the organic phase, AcAc : acetyl acetone, n number of ligands L.

Experimental

Reagents and Solutions :

All chemicals were analytical grade reagents, BDH and Merck.

(a) The aqueous phase contains sodium acetate and acetic acid each 0.2*M* present in the proper ratio to give the required *p*H while keeping the ionic strength constant at 0.2*M*. It also contains $CoCl_2 . 6H_2O$ at concentrations ranging from $10^{-2}M$ to $10^{-3}M$.

(b) The organic phase was xylene 0.1*M* in acetyl acetone (AcAc) and with different molarities of the amines (0.01-0.5*M*). The amines used were : pyridine (Py) ; 2,2'-dipyridyl (dipy) ; benzylamine (BA), dibenzylamine (DBA), triethylamine (TEA), tri-*n*-propylamine (TPrA), tri-isooctylamine (TIOA) tribenzylamine (TBA).

Procedure :

Equal volumes of the 2 phases were shaken together till equilibrium, after separation the cobalt was determined complexometrically in the two phases.

Calculation of the formation constant $K_{2,n}$:

The species extracted are neutral complexes. The distribution ratio

$$D = \frac{\text{Total concentration of Co(II) in the organic phase}}{\text{Total concentration of Co(II) in the aqueous phase}}$$

Using the equation given by Akaiwa and Kawanoto, $K_{2,n}$ for the 2 : n adduct Co(AcAc)

$$B_n = \frac{[Co(AcAc)_2 B_n]_o}{[Co(AcAc)_2]_o [B]^n_o} \quad \dots \quad (1)$$

This equation can be transformed to

$$\log\left(\frac{D}{D_o} - 1\right) = \log \Sigma_{n-1} K_{2,n}[B]^n_o \quad \dots \quad (2)$$

where D_o is the distribution ratio in the absence of base. Values of D_o can be obtained from the following equation :

$$K_o = D_o \frac{[H]^n}{[HA]^n}$$

where. K_o the equilibrium constant, HA the chelating acid (AcAc), n : number of base. To determine $K_{2,n}$ it is sufficient to find D at various *p*H and at various base concentrations.

Results and Discussion

The dependence on *p*H of the extraction of $Co(AcAc)_2$ for different bases is represented in Fig. 1. Increasing the *p*H, increases the precentage extraction, all bases give enhancement except TIOA, TBA. This may be attributed to the steric effect of these bases.

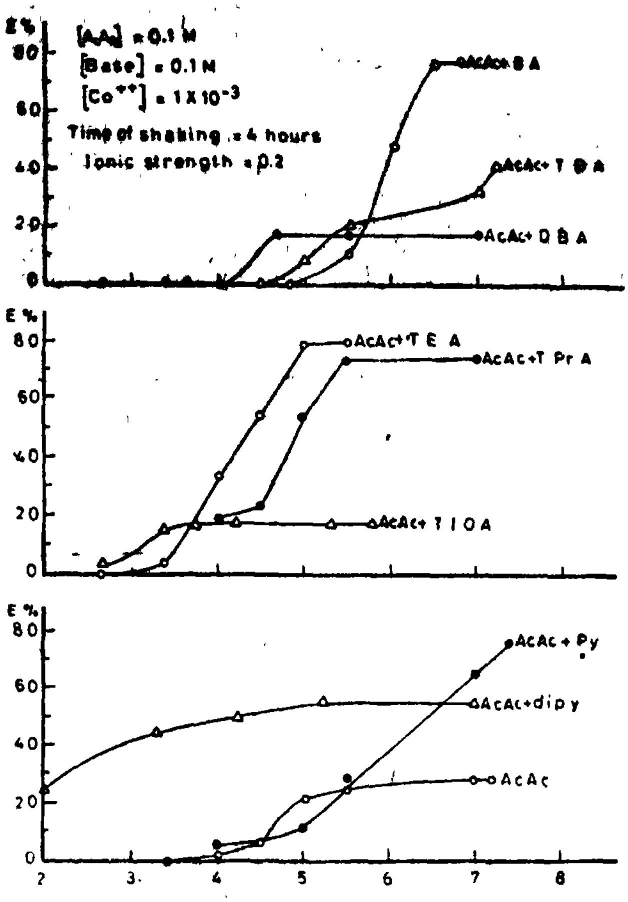


Fig. 1. Effect of pH and different organic bases on extraction of Co(II) acetylacetone in xylene.

Effect of base concentration on synergism :

Keeping AcAc at $10^{-1}M$ and Co(II) at $10^{-3}M$, the effect of the solution and the concentration ratio of the added organic base on the distribution ratio of $Co(AcAc)_2$, at room temperature, was investigated and the results are represented graphically in Figs. 2-5 for the different bases.

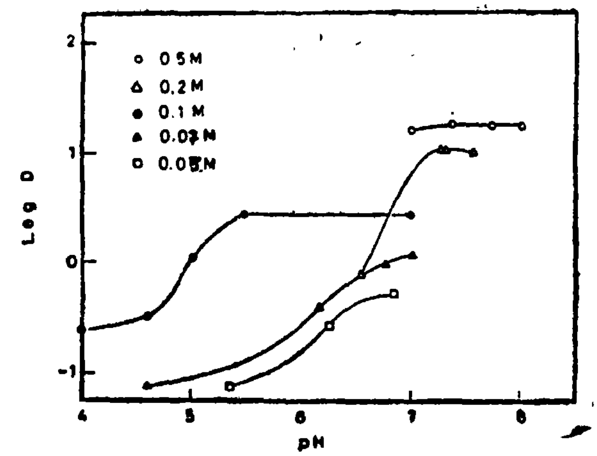


Fig. 2. Effect of pH and concentration of TPrA on extn. of $CO(AcAc)_2$ in xylene.

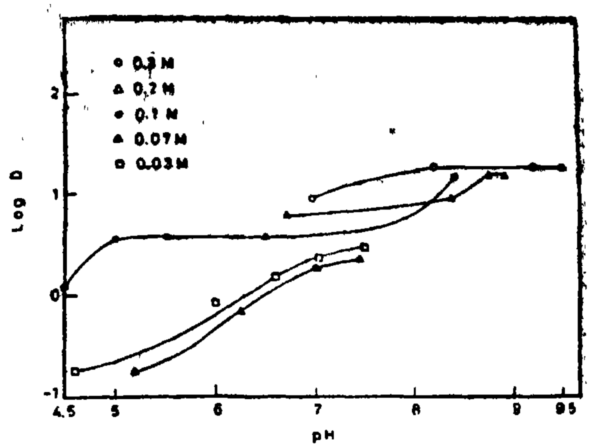


Fig. 3. Effect of pH and concentration of TEA on extraction of $Co(AcAc)_2$ in xylene.

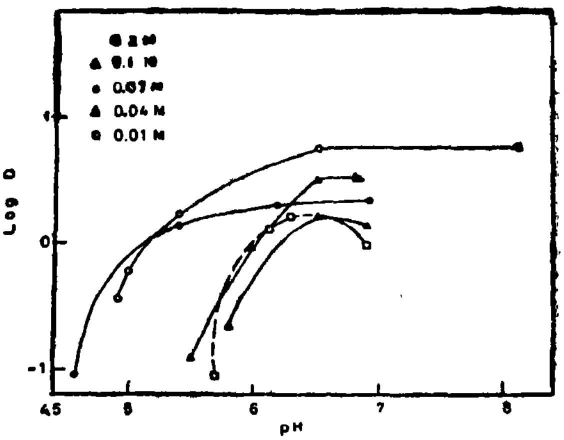


Fig. 4. Effect of pH and concentration of BA on extraction of $Co(AcAc)_2$ in xylene.

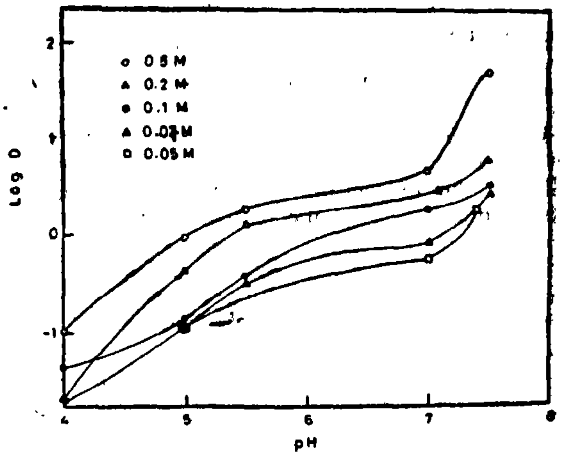


Fig. 5. Effect of pH and concentration of pyridine on extn. of $Co(AcAc)_2$ in xylene.

From these Figs. at fixed pH value (say $p\text{H}=7$) where $D_0=0.3891$, the value of log D and hence $\log\left(\frac{D}{D_0}-1\right)$ for each base can be evaluated.

Hence from equation (2), a plot of $\log\left(\frac{D}{D_0}-1\right)$ vs $\log [B]_{total}$ can be obtained and should yield a straight line, with slope n and intercept $K_{s,n}$ which is the formation constant of the reaction

$$Co(AcAc)_2+nB \rightleftharpoons Co(AcAc)_2B_n$$

Such a relation is represented in Fig. 6.

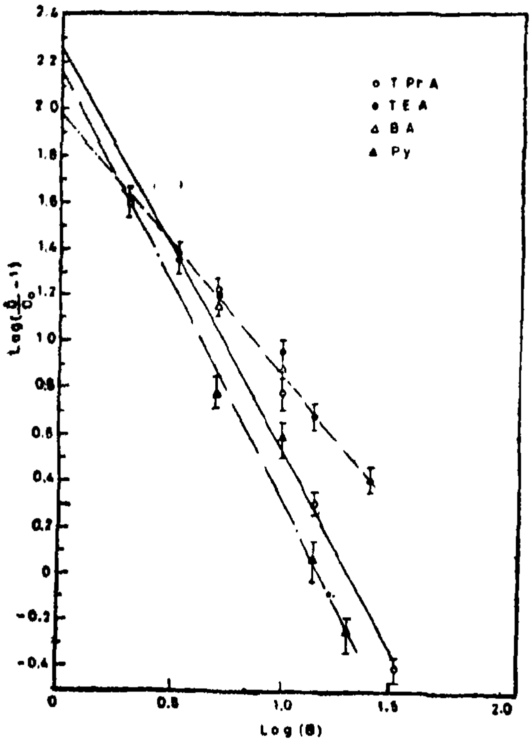


Fig. 6. Log $\left(\frac{D}{D_0}-1\right)$ vs Log $(B)_{total}$ for determination of log $K_{s,n}$ in xylene.

To increase the organic character of the Co(II) acetyl acetonate complex a base is added and this enhances the extraction of the complex in the organic phase. The mechanism by which the neutral amine adds to the metal chelate in the organic phase depends upon the nature of the complex in the organic phase.

The results indicate that for the *p*H range 6.5-7.2, the formation constants K of the adducts are almost constant. However, the number of base molecules added is only one for BA and TEA, this may be due to the bulky size of TEA causing large steric hindrance and giving a very weak bond with the $Co(AcAc)_2$ complex. But Py and TPrA both give di-adducts.

Base	pK_b	log K	n	mean log K
Py	8.82	2.12	2	2.12±0.02
TPrA	3.35	2.22	2	2.22±0.02
BA	4.66	1.97	1	1.87±0.13
TEA	3.22	1.96	1	1.86±0.13

Excess base does not change the identity or stability of the adduct.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 693-697

Kinetics and Mechanism of Oxidation of Diphenyl Sulfoxide by Sodium N-Chloro 4-Methyl Benzene Sulfonamide in Presence of Hydrochloric Acid

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Manuscript received 3 July 1979, revised 15 March 1980, accepted 9 April 1980

The kinetics of oxidation of diphenyl sulfoxide (DPSO) by sodium N-chloro 4-methyl benzene sulfonamide or chloramine-T (CAT) is studied at 40° in HCl medium. The product is diphenyl sulfone. The rate law is found to be, $-d[CAT]/dt = k[CAT][H^+]$. Ionic strength of the medium and addition of *p*-toluene sulfonamide have no effect, but chloride ion catalyses the reaction, showing that the rate law is of the form :

$$-d[CAT]/dt = k_1[CAT][H^+] + k_2[CAT][Cl^-]^{0.8}$$

The observed rate law is interpreted in terms of a fast interaction between DPSO and H_2OCl^+ formed from the hydrolysis of N-chloro *p*-toluene sulfonamide in a slow step or from the hydrolysis of Cl_2 formed from the free acid and added Cl^- ion.

MECHANISMS of many oxidation reactions of sodium N-chloro-4-methyl benzene sulfonamide, *p*-CH_3-$C_6H_4SO_2NClNa.3H_2O$ commonly called chloramine-T (CAT) have been kinetically investigated[1-16]. This reagent can oxidise compounds containing S–O bonds to the respective sulfones[16]. We have reported on the kinetics of oxidation of dimethyl sulfoxide by CAT in aqueous solution[17]. Studies on a mixed sulfoxide, namely, phenyl methyl sulfoxide have been made recently[18]. It was found worthwhile to study the oxidation of diphenyl sulfoxide (DPSO) by CAT in presence of HCl (0.04-0.08*M*). It may be mentioned that kinetic investigations on the oxidation of an aromatic sulfoxide by CAT have not been reported in literature.

Experimental

Diphenyl sulfoxide (Fluka AG) was used without further purification. A solution of the compound was prepared *in ethanol water* (50 : 50, v/v) mixture. Other experimental details are similar to those described in the previous communication[17]. The reaction was sluggish in acid medium at 0°. Hence all rate studies were made at 40°. Pseudo first order conditions were maintained and the kinetics were followed nearly to three half lives. The first order rate constants evaluated by the graphical method were reproducible within ±3%.

Stoichiometry :

Reaction mixtures containing excess CAT over DPSO were kept at room temperature (30±2°) in presence of 0.04–0.08 *M* HCl for 24 hours. Estimation of the unreacted CAT showed that one mole of DPSO consumed one mole of CAT.

$$CH_3-C_6H_4SO_2NCl\ Na + (C_6H_5)_2SO + H_2O \rightarrow CH_3-C_6H_4SO_2NH_2 + (C_6H_5)_2SO_2 + NaCl$$

The sulfonamide was identified by paper chromatography. Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution in ether as the spray reagent (R_F = 0.905). Presence of diphenyl sulfone was detected by the tlc technique. A mixture of petroleum ether (60-80°) chloroform and butanol (1 : 1 : 1, v/v) was the solvent and concentrated H_2SO_4 was used as the spray reagent (R_F = 0.52).

Results

At constant $[H^+]$, with the substrate in large excess, plots of log[CAT] vs time are linear indicating first order dependence of rate on [CAT] (Fig. 1). The pseudo first order rate constants k_1 are unaffected by an increase in substrate concentration (Table 1). Hence the rate is independent of DPSO. The reaction is acid catalysed and at constant $[Cl^-]$, shows a first order dependence on $[H^+]$ (Table 2). A plot of log k_1 vs. log$[H^+]$ gives a straight line slope 0.98. At constant$[H^+]$, addition of Cl^- in the form of NaCl (Table-3) increases the rate and a plot log k_1 vs log$[Cl^-]$ gives a straight line of slope 0.80. When the catalysis is effected simultaneously by H^+ and Cl^-, an order of 1.8 on the gross concentration of HCl is observed, indicating

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that two different mechanistic pathways are involved.

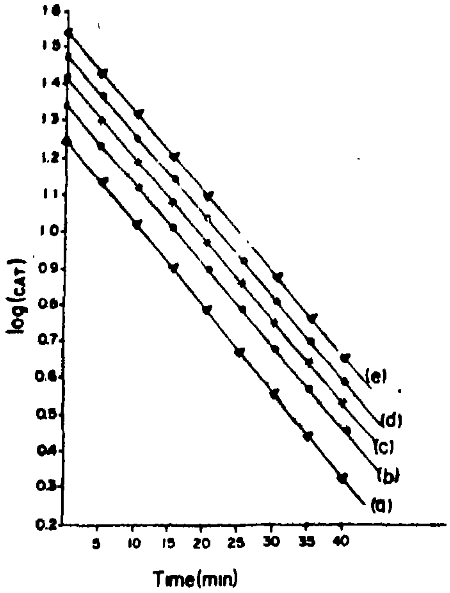


Fig. 1. Plots of log (a-x) vs time for the oxidation of DPSO by CAT. [HCl] = 0.1 M; [DPSO] = 0.1 M; μ = 0.5 M; Temp.: 40°C, [CAT] = 0.004 M (a), 0.005 M (b), 0.006 M (c), 0.007 M (d), 0.008 M (e), [EtOH] = 35%.

TABLE 1—EFFECT OF REACTANT CONCENTRATION ON REACTION RATE AT 40°C

$[H^+]$ = 0.04M $10^3[CAT]_0M$	[EtOH] = 35% $[DPSO]_0M$	μ = 0.5M $10^4k_1 sec^{-1}$
4.0	0.10	8.48
5.0	0.10	8.49
6.0	0.10	8.41
7.0	0.10	8.38
8.0	0.10	8.38
5.0	0.15	8.34
5.0	0.20	8.40
5.0	0.25	8.36
5.0	0.30	8 37

TABLE 2—EFFECT OF HYDROGEN ION CONCENTRATION ON REACTION RATE AT 40°C

$[CAT]_0$ = 0.005M; $[DPSO]_0$ = 0.1M; [EtOH] = 35%; $[Cl^-]$ = 0.08M; μ = 0.5M.

$10^2[H^+]M$	$10^4k_1 sec^{-1}$	$10^2k_1/[H^+]$
4.0	14.75	36.87
5.0	18.19	36.37
6.0	22.49	37.47
7.0	25.83	36.90
8.0	29.20	36.50

Effect of varying the Dielectric constant:

The first order rate constant k_1 was affected by variation of ethanol in the ethanol-water content of the reaction mixture. With [ethanol] = 30.0, 35.0, 40.0, 48.0, 55.0 and 60%, 10^4k_1 sec^{-1} values were 8.86, 8.49, 8.13, 7.45, 6.81 and 6.36 respectively. A plot of log k_1 vs $\frac{1}{D}$ (dielectric constant values were taken from literature[19,20]) gives a straight line with a negative slope (Fig. 2).

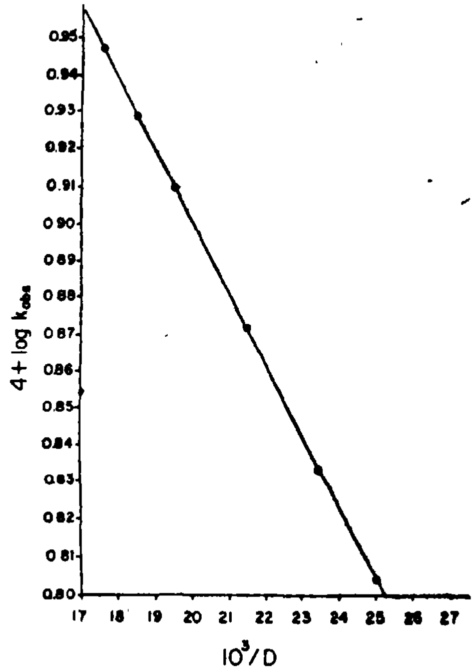


Fig. 2. Plot of log k_{obs} vs 1/D for the oxidation of DPSO by CAT in presence of HCl. [HCl] = 0.1 M; [DPSO] = 0.1 M; μ = 0.5 M; Temp.: 40°C [CAT] = 0.005M.

Effect of Neutral salts:

Increase in ionic strength of the medium from 0.5 to 0.8 using $NaClO_4$ affected k_1 only marginally (Table 3).

TABLE 3—EFFECT OF IONIC STRENGTH AND TOTAL CHLORIDE ION CONCENTRATION ON REACTION RATE AT 40°C

$[CAT]_0$ = 0.005M; $[DPSO]_0$ = 0.1M; $[H^+]$ = 0.04M; [EtOH] = 35%

$[NaClO_4]$	$10^4k_1 sec^{-1}$	$10^2[Cl^-]M$	$10^4k_1 sec^{-1}$
0.5	2.99	5.0	10.04
0.6	3.24	5.5	11.07
0.8	3.40	6.0	11.72
		7.0	13.41
		8.0	14.75

Effect of p-*toluene Sulfonamide:*

Addition of p-toluene sulfonamide (TSA) had negligible effect on the rate. With 10^3[TSA] = 0.0,

5.0, 10.0 and 20.0, values of $10^4 k_1$ were 8.4, 8.3, 8.2 and 8.2 sec^{-1}.

TABLE 4—EFFECT OF TEMPERATURE ON REACTION RATE

$[CAT]_0 = 0.005M$; $[DPSO]_0 = 0.1M$; $[H^+] = 0.04M$; $\mu = 0.5M$; $[EtOH]_0 = 35\%$

Temperature °K	313.0	318.0	323.0	328.0
$10^4 k_1 sec^{-1}$	8.49	11.51	16.88	21.14

Effect of Temperature :

Kinetic runs were made at different temperatures (Table 4) and the activation parameters have been evaluated : $E_a = 52.3$ kJ $mole^{-1}$; $\Delta H^{\neq} = 48.96$ kJ $mole^{-1}$; $\Delta S^{\neq} = -147.4$ JK^{-1}, $\Delta G^{\neq} = 95.0$ kJ $mole^{-1}$.

Evaluation of parameters under conditions, $[CAT] = 6.0\times10^{-3}M$; $[DPSO] = 0.15M$; $[HCl] = 0.020M$; $[EtOH] = 35\%$ also gave identical results.

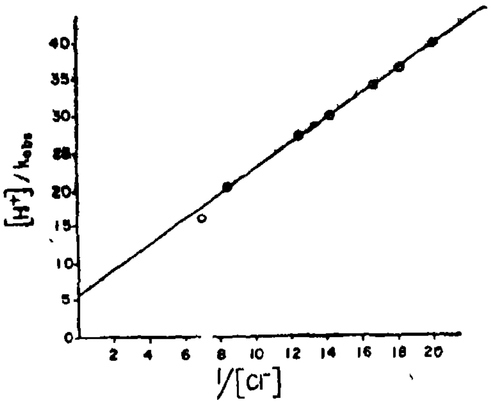


Fig. 3. Plot of $[H^+]/k_{obs}$ vs $1/[Cl^-]$ for the oxidation of DPSO by CAT in presence of HCl. $[HCl] = 0.1\ M$; $[DPSO] = 0.1$; M; $\mu = 0.5\ M$; Temp.: 40°C $[CAT] = 0.005\ M$. $[EtOH] = 35\%$.

Discussion

The rate of oxidation of DPSO by CAT depends on [CAT] and $[H^+]$. This is in contrast to our observations with the oxidation of dimethyl sulfoxide[17] by CAT, where in addition, a first order dependence of rate on the substrate concentration was noted. Introduction of the phenyl group probably increases the electron density at the hetero atom facilitating electrophilic attack by the positive halogen of oxidant[18].

Protonation of DPSO is of little importance at low acidities as shown by Oae *et al*[21]. On the other hand, protonation of CAT has been thoroughly investigated by Morris *et al.*[22] and Higuchi and coworkers[23]. Chloramine-T ionizes in aqueous solution as[24] :

$$RNCl\ Na \rightleftharpoons RNCl^- + Na^+, \text{ where } R = p\text{-}MeC_6H_4SO_2$$

The anion picks up a proton in acid solution to give the free acid RNHCl. The acid can undergo disproportionation and/or hydrolysis producing dichloramine-T ($RNCl_2$) and HOCl. Thus the probable oxidizing species in acidified CAT solutions are $RNCl_2$, RNHCl and HOCl. If $RNCl_2$ were to be the reactive species, a second order dependence of rate on CAT is predicted from equation (1), which is contrary to the present experimental observations :

$$2\ RNHCl \rightleftharpoons RNCl_2 + RNH_2 \quad \ldots \quad (1)$$

With RNHCl or HOCl, Schemes-I and II can be proposed for the oxidation of DPSO by CAT.

$$RNCl^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RNHCl \quad \ldots \text{(i) Slow and forward reaction is rate determining.}$$

$$RNHCl + DPSO \xrightarrow{k_2} Products \quad \ldots \text{(ii) Fast.}$$

SCHEME-I

$$RNCl^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RNHCl \quad \ldots \text{(i)}$$

$$RNHCl + H_2O \xrightarrow{k_2} RNH_2 + HOCl \ldots \text{(ii) Slow and rate determining}$$

$$HOCl + H^+ \xrightarrow{k_3} H_2OCl^+ \ldots \text{(iii) Fast}$$

$$H_2OCl^+ + DPSO \longrightarrow Products \ldots \text{(iv) Fast.}$$

SCHEME-II

Scheme-I envisages the direct participation of RNHCl in a rate determining step. With the steady state approximation for RNHCl and assuming $k_2 [S] > k_{-1}$, the rate law,

$$\frac{d[CAT]}{dt} = k_1[CAT][H^+] \quad \ldots \quad (2)$$

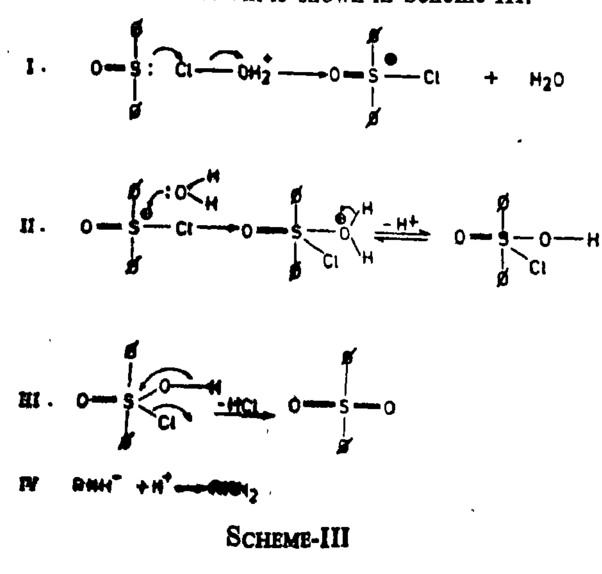
in agreement with experimental results can be derived. In Scheme-II, formation of HOCl takes place in a slow step through the hydrolysis of RNHCl, and is followed by a rapid protonation and reaction with the substrate. Rate law (2) can be derived by invoking steady state conditions for the intermediates and assuming $k_1[CAT][H^+] \gg k_{-2}[RNH_2][HOCl]$.

First approximation calculations by Bishop and Jennings[24] on decinormal solutions of CAT have shown that concentrations of RNHCl and HOCl are approximately 10^{-2} and $10^{-7}M$ respectively, around pH 0-1. Although the concentration of former species is larger, Pryde and Soper[25] have shown that interaction of RNHCl with the substrates could be slow, while HOCl would attack at a faster rate. Protonation converts the latter into a stronger electrophile than the precursor RNHCl, and it can attack the sulfoxide at a faster rate. Absence of significant ionic strength effect on the rate rules out the involvement of ions in a rate determining step (i.e., Scheme-I). Further, a change in the solvent composition by varying the ethanol content in ethanol-water affects the reaction rate. The general equation relating to the effect of dielectric constant D to the reaction velocity in a bimolecular reaction has been derived by Landskroener and Laidler[26]. For the limiting case of zero angle of approach between two dipoles, Amis[27] has shown that

$$\ln k'_D = \ln k'_{D\infty} - 2\mu_1\mu_2/DkTr^3 \quad \ldots \quad (3)$$

where k'_D is a function of dielectric constant D, μ_1 and μ_2 are the dipole moments of the reactants, r is the distance of approach for the two dipoles, k is the Boltzman constant and T is the absolute temperature. Equation (3) predicts a linear relation between log k_{obs} and $\frac{1}{D}$. The slope of the line should be negative for a reaction between two dipolar molecules, while a positive slope is obtained for ion-dipole reactions. In the present investigations, the plot of log k_{obs} vs $\frac{1}{D}$ is linear with a negative slope, thus supporting the participation of two dipolar species in Step (ii) of Scheme-II.

A detailed mechanism of oxidation of DPSO by CAT in acid medium is shown in Scheme-III.



SCHEME-III

In Scheme-III, an electrophilic attack by the positive chlorine of H_2OCl^+ at the sulphur atom in the substrate is envisaged. A considerable degree of nucleophilicity is expected at this site because of the extended electron density due to $p\pi$-$d\pi$ overlap in the S—O bond and the presence of two phenyl rings in the molecule. The reaction intermediate formed in Step (I) hydrolyses through a fast step.

Values of the energy of activation and $\Delta S^{\neq}$ are comparable with those obtained during the oxidation of conjugated alcohols[10], with CAT, where similar kinetics have been observed. The activation parameters are probably related to the protonation equilibria and the subsequent hydrolysis step (Scheme-II). Protonation of $RNCl^-$ ion converts a more or less linear structure into a pyramidal arrangement and the sign of $\Delta S^{\neq}$ confirms the formation of such a compact structure.

Effect of Chloride ion :

The rate increases in presence of added chloride ion (Table 3) though a fractional order dependence (0.80) on the $[Cl^-]$ is seen. Such behaviour has been noted in the Orton rearrangement[28] of organic haloamides. The attacking species under these conditions will be either molecular chlorine formed by the interaction of RNHCl and Cl^- ion or HOCl formed in the hydrolysis of the former species. The observed kinetic behaviour can be explained by Scheme-IV.

$$RNCl^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RNHCl \quad \ldots \quad \text{(i) (Slow)}$$

$$RNHCl + Cl^- \xrightarrow{k_2} RNH^- + Cl_2 \quad \ldots \quad \text{(ii) Slow and rate determining.}$$

$$Cl_2 + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HOCl + H^+ + Cl^- \quad \ldots \quad \text{(iii) Fast}$$

$$HOCl + H^+ \xrightarrow{k_4} H_2OCl^+ \quad \ldots \quad \text{(iv) Fast}$$

$$H_2OCl^+ + DPSO \xrightarrow{k_5} \text{Products} \quad \ldots \quad \text{(v) Fast}$$

$$RNH^- + H^+ \xrightarrow{k_6} RNH_2 \quad \ldots \quad \text{(vi) Fast}$$

SCHEME IV

Applying steady state conditions for RNHCl, it can be shown that

$$-\frac{d[CAT]}{dt} = \frac{k_1k_2[CAT][H^+][Cl^-]}{k_{-1}+k_2[Cl^-]} \quad \ldots \quad (4)$$

Under conditions $k_{-1} \gg k_2 [Cl^-]$, the rate expression becomes

$$-\frac{d[CAT]}{dt} = \frac{k_1 k_2}{k_{-1}} [CAT][H^+][Cl^-] \quad \dots \quad (5)$$

indicating a first order dependence of the rate in $[Cl^-]$. If $k_{-1} \ll k_2[Cl^-]$, the rate expression becomes

$$-\frac{d[CAT]}{dt} = k_1 [CAT][H^+] \quad \dots \quad (6)$$

The rate becomes independent of the chloride ion concentration. However, if $k_{-1} \approx k_2 [Cl^-]$, the order becomes fractional with respect to $[Cl^-]$, i.e., 0.8, in this case, as observed experimentally which is similar to Euler's case I(c)[29].

Equation (4) can be transformed into (7) and (8)

$$k_{obs}[CAT] = \frac{k_1 k_2 [CAT][H^+][Cl^-]}{k_{-1} + k_2 [Cl^-]} \quad \dots \quad (7)$$

$$\frac{[H^+]}{k_{obs}} = \frac{k_{-1}}{k_1 k_2 [Cl]} + \frac{1}{k_1} \quad \dots \quad (8)$$

A plot of $[H^+]/k_{obs}$ vs $1/[Cl^-]$ gives a straight line (Fig. 3). If $K = k_1/k_{-1} = 2.8 \times 10^{-5}$ at 25° (Morris *et al*[22]), from the slope and intercept of the line, $k_2 = 1.64 \times 10^{-5}$ sec^{-1} and $k_{-1} = 5.1 \times 10^{-6}$ sec^{1-}.

Acknowledgement

One of us (M.B.J) thanks the University Grants Commission, New Delhi, for a fellowship under the Faculty Improvement Programme.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp.698-700

Kinetics and Mechanism of Polarographic Reduction of Orange II

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Manuscript received 4 December 1978, revised 6 September 1979, accepted 4 March 1980

The polarographic reduction of orange II has been studied in McIlvaine buffer (subsequently referred to as McI). The electrode process is irreversible at $pH > 4$ while in more acidic solutions the process appears tending towards reversibility. The potential dependent rate constant, $k_{f,h}$ and the kinetic parameter, 'αn_a', (the product of transfer coefficient and the number of electrons involved in the rate determining step) have been calculated. Attempt has also been made to estimate 'n_a' and to give the mechanism of electrode process.

POLAROGRAPHY of azo-dyes including orange II has been attempted by early workers[1-4]. These studies have dealt with the determination of half-wave potentials in different *p*H values for the purpose of identification and variation of half-wave potentials with the substitution in benzene rings. In the present study an attempt has been made to study the kinetics of the electrode process and to give a probable mechanism of the electrode process. The above mentioned parameters have been calculated under varying conditions of *p*H wherever the general nature of the current voltage curves are commensurate with the quantitative calculations.

Experimental

The dropping mercury electrode (d.m.e.) consisted of a standard capillary (E. H. Sargent Co., U.S.A.). The polarographic cell was thermostated at $25° \pm 0.1°$. The d.m.e. had the following capillary characteristics $m = 1.852$ mg/sec, $t = 3.5$ sec, $m^{2/3} t^{1/6} = 1.858\ mg^{2/3}\ sec^{-1/2}$ (in 1.0*M* $NaClO_4$, at -0.60 V vs S.C.E.). The various heights of the mercury head corrected for back pressure were 34.3, 54.3, 74.3, 94.3 and 104.3 cm. 1.0 *M* $NaClO_4$ was used as the supporting electrolyte. The resultant concentration of depolarizer was kept 1.0×10^{-3} *M* in each case. Gelation (1×10^{-3}%) was used as the maximum suppressor. Deoxygenation, preparation of solutions etc. were as reported earlier[5].

Results

(i) *Current-potential Curves* :

Fig. 1 gives the current-voltage curves at different *p*H values. A sudden and significant shift in the wave towards more negative potentials is observed from *p*H 4 to *p*H 5 followed by a gradual shift in the same direction as the *p*H is increased. At *p*H 5 the wave appears to be in two pars ; the main wave being preceded by a prewave.

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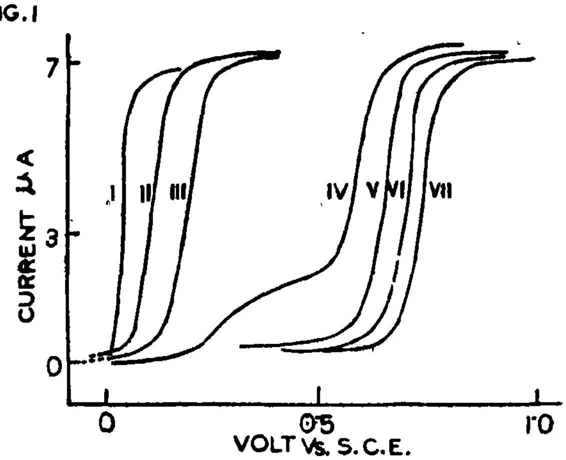


Fig. 1. Polarograms of Orange II at different *p*H values, I, 2.2 ; II, 3.0 ; III, 4.0 ; IV, 5.0 ; V, 6.0 ; VI, 7.0 ; VII, 8.0.

The nature of the prewave has been ascertained from the study of current-time (c-*t*) curves which are shown in Fig. 2. From the inspection of these curves it is evident that a large disturbance occurs at the interface as the c-t curves are no more symmetrical (deviating from the dotted curves in Fig. 2) and are irregular. These c-t curves resemble the adsorption prewave for the adsorption of reduction product in reversible systems.

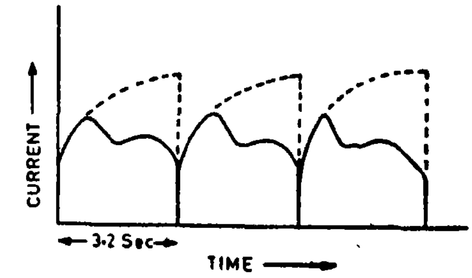


Fig. 2

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Value of 'n' :

The number of electrons involved in the electrode process is a necessary prerequisite for the mechanism and though since long for an azo group ("-N=N-") it has been known[6,7] to be 2, this was experimentally ascertained by coulometry[8] as well as by direct determination of diffusion coefficient[9]. At all the pH values it was found to be 2 within the limits of experimental error.

Irreversibility test :

If α in relation $E_{3/4} - E_{1/4} = 0.0564/\alpha n$ (at 25°) is less than 0.5 the electrode process is said to be totally irreversible[10]. A more rigorous test of irreversibility depends upon the variation of limiting current upon the height of the mercury column[11]. The results are shown in Fig. 3. This indicates that at the foot of the wave (i.e., at 0.60 volts vs S.C.E.) the limiting current is independent of height of the mercury column i.e., it is entirely determined by the rate of the electrode process while at the top of the wave (i.e., at 0.8 volts vs S C.E.) it is independent of the rate of electrode process and is entirely determined by diffusion. And between the two extremes both rate of electrode process as well as diffusion determine the magnitude of the current. Influence of the former gradually decreases while that of latter gradually increases as one moves up the wave.

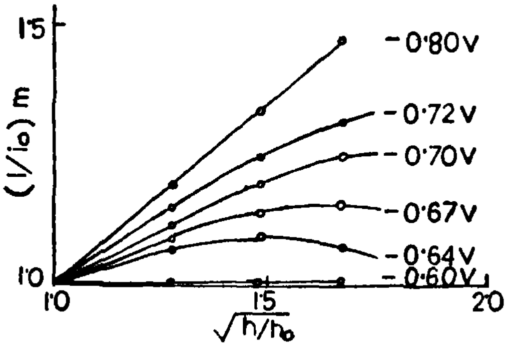


Fig. 3

Kinetic parameter :

The rate constant has been calculated by the method of Koutecky[12] and then a plot of variation of rate constant with potential in the range 0.1 < i/i_d > 0.94, yields αn_a. The results are given in Table 1

Mechanism :

In acid solution azo nitrogen takes up a proton to give a structure which is a resonance hybrid of two

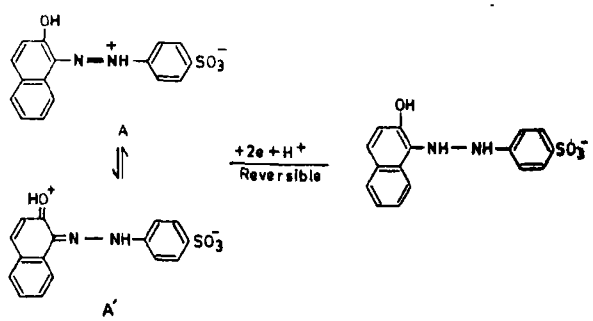
TABLE 1—POLAROGRAPHIC DATA OF ORANGE II IN McILVAINE BUFFER

[Orange II] = $1 \times 10^{-3} M$; [$NaClO_4$] = 1.0M ; μ = 1.0; Temp. 25±0.1°C

pH	$-E_{1/2}$ V S.C.E.	$-(E_{3/4}-E_{1/4})$ V S.C.E.	α	αn_a
2.2	0.035	0.025	~ 1	-
3.0	0.045	0.045	>0.5	-
4.0	0.195	0.060	<0.5	0.85
6.0	0.650	0.060	<0.5	0.92
7.0	0.690	0.060	<0 5	1.00
8.0	0.730	0.060	<0.5	0.97

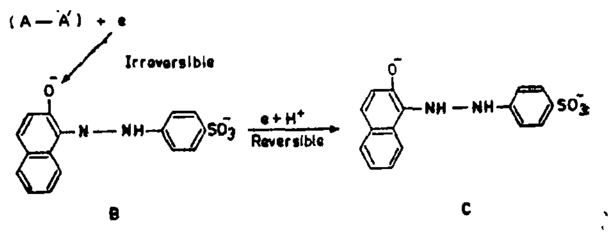
extreme structures[13] A-A'. Grabbing of a proton makes -N=N- an electrophile. However, strong acidity may prevent dislodging of phenolic hydrogen. As the pH is increased, though still remaining acidic, this electrophilic effect probably dislodges the phenolic hydrogen as the first step to give structure B. In alkaline medium because of ionization of phenolic hydrogen the depolarizer has the resonating structure C.

The structure (A—A') is electron seeking and thus it is likely that 2 electrons are taken up in a fast reversible step

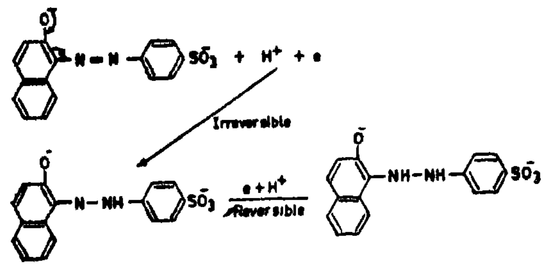


An attempt to estimate n_a from αn_a values leads to n_a = 2 because for irreversible system α<0.5. According to Meites[14] only a single electron can be transferred at a time and a value of n_a exceeding 1 should merely mean that the successive steps are too nearly simultaneous to be distinguished on the time scale implicit in a polarographic measurement.

The irreversible reduction in acidic medium may be represented to occur as



In structure C because of the excess negative charge density, the electron take up is likely to be relatively difficult. Probably in the first slower step, one proton and one electron is taken up which opposes the flow of electron from the phenolic oxygen and gives as intermediate free radical which then in a fast reaction takes up another electron and proton to give the final product.



Acknowledgement

Thanks are due to Dr. S. N. Srivastava, Principal, Agra College, Agra for providing necessary facilities.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 701-704

Conductance Study of Mixed Halocobaltates(II) in Acetonitrile

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Manuscript received 19 October 1978, accepted 9 April 1980

The values of molar conductance of some mixed tri-, mixed tetra- and mixed pentahalocobaltates(II) at single concentration have been found out which indicate that these compounds behave as 1 : 1, 2 : 1 and 3 : 1 electrolytes respectively in solution ; for mixed tetra- and mixed pentahalocobaltates(II) these conclusions are in contrast to those from electronic andfar i.r. spectral behaviour. An explanation for this anomaly has been advanced. For the mixed trihalocobaltates(II) equivalent conductance has been found out at different concentrations and Debye-Hückel-Onsager equation has been applied to confirm the 1 : 1 electrolyte nature. The calculated and experimental slopes of the plots of $\Lambda_0 - \Lambda_e$ vs $\sqrt{c}$ have been compared.**

WE have recently isolated and characterized a few mixed** halocobaltates (II)[1-5]. Apart from electronic spectral, far i.r. and magnetic studies which we have already reported, we have now carried out conductance measurements of these complexes in acetonitrile which are being reported in the present article. Use of conductance measurements in the study of coordination complexes has been, for long, in vogue for the characterization of the electrolyte type, and therefore, to some extent, the structure of the complex in solution. Most of the coductance data reported in literature to characterize a given coordination compound are at a fixed concentration ($\sim 10^{-3}M$) but recently this method has been critisized[6], and measurement fo conductance over a range of concentration has been suggested to arrive at unambiguous results. In the present work measurements were made at fixed concentration for all the three types of mixed halocobaltates (II), namely mixed tri-, tetra- and pentahalocobaltates (II) but measurements over a range of concentration were made only for mixed trihalocobaltates (II). The reason for this choice is discussed later.

Experimental

The methods of preparation of the complexes have already been reported[1,2,5]. All measurements were carried out on a WG Pye conductance unit. A conductance cell with lightly platinized electrode was used. It was standardized by a standard solution of A. R. potassium chloride. BDH acetonitrile was purified by the method of Walden and Birr[7] ; the specific conductance of the purified solvent was found to be 2×10^{-7} mhos cm^{-1} (reported value 5.9×10^{-8} mhos cm^{-1})[6]. Conductance of all the complexes were measured at 25±0 5° at $1\times10^{-3}M$ and $2\times10^{-3}M$ concentrations. For trihalocobaltates (II) the measurements were carried out at different concentrations in the range 10^{-2} to 10^{-4} eq/l at 25±0.5°.

Treatment of Data :

Molar conductance :

Λ_M at single concentration was calculated by using the equation $\Lambda_M = \frac{1000k}{c}$ ... (1)

where k is specific conductance and c is molarity of the solution.

Debye-Hückel-Onsager equation[8] :

The equation $\Lambda e = \Lambda o-(A+B\Lambda o\omega)\sqrt{c}$ ... (2) was used for analysing the data obtained at different concentrations where the symbols have their usual significance.

First Λ_e values were plotted against $\sqrt{c}$ and the linear portion of the plot was extrapolated to zero concentration to obtain Λ_0 value. Equation (2) on rearrangement gives

$$\Lambda o-\Lambda e=(A+B\Lambda o\omega)\sqrt{c} \quad ... (3)$$

The slope of the line obtained by plotting ($\Lambda o-\Lambda e$) against $\sqrt{c}$ gave the experimental value of the factor ($A+B\Lambda o\omega$) which was compared with the theoretically calculated value of this factor to give an idea about the type of electrolyte under study. This factor was calculated from the expressions for A,B and ω[8]. In calculating ω for a 1 : 1 electrolyte λ_0^+ and λ_0^-, the limiting ionic mobilities of the cation

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**The term "mixed" is applied to halocobaltates(II) having more than one kind of halogens e.g., $CoCl_2Br^{2-}{}_2$ and "simple" to those having only one kind of halogen e.g., $CoCl^{2-}{}_4$.

and anion respectively need not be known as they cancel out in the calculation.

TABLE 2—PARAMETERS FOR DEBYE-HÜCKEL-ONSAGER EQUATION

Temperature : 25±0.5°C, η=0.345 centipoise, D=36.7, E=$(C_2H_5)_4N^+$

Compound	Λ_0	A	B	ω	Slope (exp.)	Slope (cal.)	Slope (exp.) / Slope (cal.)
$E(CoCl_2I)$	159	228	1.224	0.586	417	342	1.22
$E(CoBr_2I)$	162.5	228	1.224	0.586	571	345	1.66

Results and Discussion

The results for single concentration measurements are given in Table 1. The parameters for Debye-Hückel-Onsagar equation and the experimental and calculated slopes are reported in Table 2 for mixed trihalocobaltates.

TABLE 1—Λ_M VALUES AT (25±0.5°)C, SOLVENT : ACETONITRILE*

B = $(n\text{-}C_4H_9)_4N^+$, ; E = $(C_2H_5)_4N^+$

Compound	Λ_M (mhos cm^{2}mol^{-1}) (Conc. 1.00 × 10^{-3}*M*)	Λ_M (mhos cm^{2}mol^{-1}) (Conc. 2.00 × 10^{-3}*M*)
$E(CoCl_2I)$	145	140
$E(CoBr_2I)$	144	137
$E_2(CoCl_4)$	316	290
$E_2(CoCl_2Br_2)$	307	284
$B_2(CoCl_2I_2)$	316	298
$E_2(CoBr_2I_2)$	350	322
$E_3(CoCl_5)$	414	390
$E_3(CoCl_3Br_2)$	357	315
$E_3(CoCl_2Br_3)$	355	315
$E_3(CoClBr_4)$	364	327
$B_3(CoCl_2I_3)$	343	303
$B_3(CoBr_2I_3)$	350	315

*Range for various electrolyte-types in this solvent are[6]

Electrolyte	Range for Λ_M
1 : 1	120-160
1 : 2	240-320
1 : 3	340-420

Single concentration molar conductance values :

From an examination of the molar conductance values at single concentration (Table 1). it is evident that they fall within the generally acceptable range of the different kinds of electrolytes in accetonitrile, thus apparently confirming the presence of ionic species manifest in the molecular formula of the respective complex. For example, Λ_M for $[(C_2H_5)_4N]_2$ $[CoCl_2Br_2]$ is 284 (mhos cm^2 mol^{-1}) which is well within the range 240-320 accepted for a (1 : 2) electrolyte in acetonitrile. The values for pentahalocobaltates (II) fall in the range of (1 : 3) electrolytes thus leading one to conclude that triply charged Co(II) would exist in solution.

These results are surprising in view of our conclusion from far i.r. and electronic spectral results that the pentahalocobaltates (II) are in fact double salts containing tetrahedral Co(II)[8] like the earlier reported Cs_3CoCl_5 being Cs_2CoCl_4. CsCl[9]. Further it has been concluded from the solution spectral results of mixed tetra-and pentahalocobaltates (II) that the solvent replaces one of the halides from the coordination sphere and thus the original species is destroyed, resulting in solution containing a mixture of species[10]. Similar observation has been reported for simple tetrahalocobaltates (II) earlier[11-13], viz. $CoCl_4^{2-}$ exists mainly as $(CoCl_3X)^-$ and Cl^- in an organic solvent. In case of mixed trihalocobaltates (II) entrance of the solvent molecule into coordination sphere does not disturb the original halides attached to Co (II) except that the bridge is broken and the fourth coordination site is occupied by a solvent molecule [A one dimensional chain type structure with bridging halogen and tetrahedrally coordinated Co (II) has been proposed for the mixed trihalocobaltates (II)[8]. Thus the value of Λ_M falling in the expected range for a particular electrolyte in case of tetra-and pentahalocobaltates (II) gives only a deceptive result about the number of ions present in the solution.

The deceptive result for the tetra- and pentahalocobaltates (II) may be explained if the following points are taken into consideration : (*i*) Tetrahalo- and pentahalocobaltates (II) dissociate in acetonitrile to give rise to mixture comprising, mainly univalent negatively charged species e.g., $CoCl_4^{2-}$ gives rise to $(CoCl_3CH_3CN)^-$ and Cl^- (a small amount of $CoCl_4^{2-}$ may also be present) and $(CoCl_4Br)^{3-}$ which has been shown to $(CoCl_3Br)^{2-}$. Cl^{-5} will give rise to $(CoCl_3CH_3CN)^-$, Br^- and Cl^- [a small amount of $(CoCl_3Br)^{2-}$ may also be present}; it may be noted that in $(CoCl_3Br)^{2-}$ bromide will be replaced from the coordination sphere by CH_3CN molecule since it is more susceptible to solvent attack than chloride[11].

(*ii*) It is known that it is not possible[14] to distinguish, by conductance measurements, between a solution containing a mixture of species and the one containing single species, if the mobilities of the ions present in the mixture and that of the single species are almost the same. Thus, taking $CoCl_4^{2-}$ as an example, which gives a mixture of $COCl_4^{2-}$ (very small amount), $(CoCl_3CH_3CN)^-$ and Cl^- in solution[11], the mobilities of the latter two ions may not be very much different from each other and this may be explained in terms of (a) the electrical field around the ion and (b) the size of the ion .A smaller ion e g., Cl^-, is expected to move faster than

$(CoCl_2CH_3CN)^-$ but it would gather more electrical field as compared to the bigger ion and thus its movement would be hampered by the ionic atmosphere of opposite charges around it. Thus a situation exists where the mobilities of the ions present in solution may not be very much different from each other. For example, a comparison of λ_0^- values of Cl^- and BCl_4^- shows that these are nearly the same (91.6 and 95.2 respectively)[15] even though the ions differ considerably in their size.

Based on the above arguments the observation that the Λ_M values for tetrahalocobaltates (II) fall in the range of (1 : 2) electrolyte inspite of its dissociation into monovalent species may be explained in the following way. In the equation (I) used for the calculation of Λ_M, concentration term is in the denominator and while calculating Λ_M for $CoCl_4^{2-}$ without taking into consideration its dissociation, the concentration used is just nearly the half of the total concentration of all the species present in the solution and that is why the expected value for a (1 : 1) electrolyte gets nearly doubled to fall in the range of a (1 : 2) electrolyte. Similarly for pentahalocobaltates (II) taking $(CoCl_3CH_3CN)^-$, Br^-, Cl^- and $(CoCl_3Br)^{2-}$ (very small amount) in solution the concentration (of monovalent species) is actually nearly thrice of what would be expected if $(CoCl_4Br)^{3-}$ were present as such and hence the value falls in the range of (1 : 3) electrolyte.

In the light of above observations it is noteworthy that some of the earlier workers[16-19] have measured the molar coductance of halometallates(II), MX_4^{2-} (M = Co, Ni ; X = Cl, Br or I) at fixed concentration in acetonitrile, nitromethane etc. and have characterized the complexes as various electrolyte types according to the accepted ranges. But in view of the solvent attack discussed above, these values do not represent the actual Λ_M values of the original tetrahedral species but instead, they represent like in the present work, Λ_M's for a mixture of species.

Conductance over a range of Concentration :

The study was limited to trihalocobaltates (II) only since, as mentioned earlier the tetra- and pentahalocobaltates (II) give rise to a mixture of species and though the magnitude of Λ_M value for the trihalocobaltates (II) was sufficient enough to characterize them as (1 : 1) electrolytes in acetonitrile solution (Table 1) the view[6] that the single concentration is frequently chosen arbitrarily and in many cases even for a series of related compounds is chosen differently, thus making the direct comparison difficult and that the method requires the assumption of a molecular weight which may well be erroneous, underscored the necessity of undertaking a study of conductance over a concentration range.

It had been mentioned earlier that trihalocobaltates (II) were shown to have a halo-bridged tetrahedral structure and a one dimensional chain structure was favoured vis-a-vis a dimeric unit structure[2]. Now, in Table 1 the value of Λ_M, to take $[(C_2H_5)_4N]\,[CoCl_2I]$ as an example, does fall in the accepted range for a (1 : 1) electrolyte, but the concentration used in calculating the Λ_M has the basis that $(CoCl_2ICH_3CN)^-$ is present in solution and had it been supposed that the dimer species $(Co_2Cl_4I_2)^{2-}$ is present in solution, the concentration term would have become half of that used in $(CoCl_2ICH_3CN)^-$ case bringing the Λ_M value within the range for a (1 : 2) electrolyte.

But in view of the chances that acetonitrile may break up the bridging bonds producing two $(CoCl_2ICH_3CN)^-$ species from one $(CoCl_4I_2)^{2-}$ species, the dimer if present in solid state, will not be present in solution and the solution will behave just as if a monomer is present in solid state and has become solvent-coordinated on putting in solvent. However, Bobbit and Gladden[20] have, by molecular weight determination of $[(C_2H_5)_4N]\,[CoCl_3]$ in acetonitrile at various concentration, shown that in solution $(Co_2Cl_6)^{2-}$ species is present. And if their results are to be believed and it is supposed that the dimer, if present in solid state, is retained in solution without any solvent attack in case of the complexes under study, the Λ_M measurement at a fixed concentration, as shown in the previous paragraph cannot distingusih between a monomer and a dimer. So, to resolve this ambiguity measurement of conductance over a range of concentration was carried out.

A comparison of the experimental and calculated values of the slope (Table 2) shows that though the former are greater than the latter (an explanation for this descrepancy is given later) the complexes at least in solution, can safely be taken to be (1 : 1) electrolyte as the theoretical value of slope for a (1 : 2) electrolyte under the same conditions and with Λ_0 as reported in Table 2 will be $\sim$700 which is far above either of the two experimental values of slopes for the complexes under study. It may be noted that lower slope value than the theoretical one should not be observed for a given type of electrolyte even when completely dissociated And even if solvent coordination by replacement of one of the halides in the coordination sphere of the possible dimer species in solution is allowed, the value of the theoretical slope may still be higher if the same equivalent weight as calculated for the dimer species is used for calculating Λ_0. Thus in the case of the mixed trihalocobaltates (II) dimeric species is not present in solution and they are (1 : 1) electrolytes.

The range of concentration used in this study was $10^{-3}-10^{-4}$ eq/l which is the range widely used by other workers[21-24]. Noticable association is observed at a higher concentration[24]. The lower

concentration range was also limited due to the experimental errors in measuring conductance[25]. An interesting feature in the plots of Λe vs $\sqrt{c}$ is that beyond ~10^{-4} eq/l linearity is lost and an upward trend in the curve is noticed. This observation may be explained by solvolysis reaction of the type

$$(CoX_3YCH_3CN)^- + mCH_3CN = [CoX_{3-n}(CH_3CN)_{m+1}]^{(m-1)-} + Y^- + nX^-$$

where n=0, 1, 2 and m=n+1.[f] Thus an increase in the number of ions causes an unusual rise in conductance. Similar phenomenon has been reported by Cotton *et al*[21].

Table 2 shows that for both the mixed trihalocobltates (II) the experimental value of the slope is greater than the theoretically calculated one for a (1 : 1) electrolyte. Such a variation is not an unusual phenomenon, particularly in non aqueous solvents and is attributable to association or incomplete dissociation of the electrolyte present in solution. When the dissociation is incomplete, the observed conductance is less than what should have been observed at that particular concentration with the result that the ratio

$$\frac{\Lambda_0 - \Lambda_e}{\sqrt{c}} = (A + B\Lambda_{0\omega})$$ increases beyond the expected value. The ratio of the experimental slope to the calculated slope is more in case of $(CoBr_3I)^-$ than in case of $(CoCl_3I)^-$ which indicates that the degree of dissociation is more for the latter. A range of similar ratios (1.038 – 1.699) has been reported by Daggett and Harkness[23] for tetraalkylammonium halides in acetonitrile.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 705-708

Studies on the Molecular Complexes of Para-benzoquinone and Amino Acids. Part I

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Manuscript received 8 September 1978, revised 29 August 1979, accepted 9 April 1980

Para-benzoquinone has been found to form pinkish-red complexes with amino acids having absorption maxima lying between 480 nm to 510 nm. The complex formation is facilitated by warming and the complexes are appreciably stable. The stiochiometry of the complexes formed between PBQ with most amino acids have been found to be 1 : 2 by Job's method of continuous variation. The stability constants of the complexes in solution have also been calculated.

QUINONES are well known for their bacteriostatic, antifungicidal, antitumor activities as well as their blood clotting properties[1]. These properties make them a potential field of further study. However, physico-chemical properties of relatively few biologically active quinones have been made. The high chemical reactivity and ability to form charge-transfer complexes[2-4] gave us impetus to study the possible charge-transfer properties of quinones with amino acids, substances of vital interest of all living matters. The present communication deals with the results of our investigations on the complex formation of amino acids with para-benzoquinone.

Experimental

Amino acids (glycine, DL-α-alanine, glutamine, γ-amino-butyric acids, valine, proline, arginine, methionine, histidine and tyrosine, except G.R.—E. Merck variety) were purified by repeated crystallization from alcohol-water and drying. *p*-Benzoquinone or PBQ (Hopkins-Williams) was purified by steam distillation which gave bright yellow crystals. The purity of the sample was checked by melting point determination.

Solutions were prepared by direct weighing. Since PBQ is only slightly soluble in water, it was dissolved in little alcohol. The aforesaid amino acids absorb in the U.V. region. PBQ absorbs strongly in U.V. region as well as in visible region. Amino acids when added to PBQ show marked change in O.D. values and generally give pinkish-red complexes with absorption maxima lying between 480 nm to 510 nm depending on the nature of the amino acids. The wave lengths of maximum absorption of different complexes are given in Table 1. The colour of the complexes becomes maximum in about 40 to 50 hours depending on the nature of the amino acids. The excess addition of amino acids depends the colour of the complexes. It is noteworthy to mention that the colour formation is facilitated on warming the solution ; no decolorization takes place on cooling which ensures the appreciable stability of the complexes. The complexes have been found to be temperature reversible. O.D. values increase on heating but decrease on cooling similar to the observations of Slifkin *et al*[5] in case of proline-chloranil complexes.

The composition of the complexes were determined by Job's method of continuous variation. Equimolar solutions were prepared by mixing PBQ and amino acids of the same strength in the ratio (1 : 11, 2 : 10 ; 10 : 2, 11 : 1) and left for equilibrium for sufficient time (usually more than 40 hours) and O.D. readings were noted at the wavelength of maximum absorption. The O.D. values of the corresponding blank solutions (having the same composition as in the original solution except the amino acids) were also measured. The stoichiometry of amino acids and PBQ complex were found in the ratio 2 : 1 in almost all cases except for Arginine PBQ (1 : 1), Tyrosine-PBQ (1 : 1) and Histidine-PBQ (1 : 2). The stoichiometry has also been supported by the conductometric measurement. The conductance values increased and became maximum when PBQ and amino acids were in the ratios noted earlier.

It is likely that 1 : 1 complexes may also be formed. However, our attempts to identify the (1 : 1) compounds by adding amino acids to the large excess of quinone proved futile.

It had been found that O.D. values increased with increase in amino acid concentrations and became constant when concentrations of amino acids were high (about 40 fold excess). The property was utilized to determine the extinction coefficients of the complexes. The O.D. values of the solutions containing 40 fold excess or more of amino acids to different concentrations of quinone were measured at the wavelength of maximum absorption. Under these conditions, the concentrations of the

complexes could be taken equal to the concentrations of quinone [except in the case of PBQ and Histidine complex (2 : 1) where the concentrations of the complex is equal to half of the concentration of quinone]. The extinction coefficients are given in Table 1.

Colorimetric Estimation of Quinone :

Though quinone absorbs in the visible region but the extinction coefficient is too small (ε_{425nm}= 25.12[6] whereas our values are ε_{450nm}=28 and ε_{500nm}=15) to utilise it for the quantitative estimation of quinone. The fact that the quinone is quantitatively converted into the molecular complexes by the addition of large excess of amino acids may be used for the colorimetric estimation of quinone. The quinone (in little alcohol) should be treated with excess of amino acids (about 50 times or more), kept at 50° in a waterbath for about 1-2 hours and the resultant solution should be quantitatively transferred to a volumetric flask and made upto the mark. From the O.D. readings of the solution and the corresponding blank at 500 nm and the extinction coefficients, determined previously, concentrations of quinone (10^{-3} to $10^{-4}M$) may be estimated. With arginine, the extinction coefficient is sufficiently high at λ=555 nm, absorption of quinone is negligibly small to be neglected and the blank determinations could also be avoided.

Determination of the Stability Constant of the Complexes :

For the determination of the stability constant of the complexes, different concentrations of PBQ [concentration range 10^{-4}—$10^{-3}(M)$] and amino acids [concentration range 10^{-1}—$10^{-2}(M)$] were mixed and kept for about 50 hours at 25°. O.D. readings of the solutions as well as the corresponding blanks were taken. The concentrations of complex were taken. The concentrat on of complexes were calculated from extinction cofficients and O.D. values.

All optical density measurements were taken with a Beckman DU 2 spectrophotometer kept at 25°. The conductance measurements were done with the aid of a Leeds-Northrup Model 4959 conductance bridge with a sensitivity of ±0.1%.

Calculation of Stability of the Complexes :

The stability constants of the complexes

$$A + 2B \rightleftharpoons C$$

can be written as $K = \dfrac{x}{(a-x)\,(b-2x)^2}$

where x=concentration of the complex formed, a and b are the initial concentrations of quinone and amino acids respectively.

Now $d_1 = \varepsilon_1\, a\, l$

and $d_2 = \varepsilon_1\,(a-x)\, l + \varepsilon_2\, x\, l$

$d_2 - d_1 = (\varepsilon_2 - \varepsilon_1)\, x\, l$

$$x = \frac{d_2 - d_1}{(\varepsilon_2 - \varepsilon_1)} \qquad \dots \qquad (1)$$

(Since l = 1 cm)

where ε_1 = extinction coefficient of quinone
ε_2 = extinction coefficient of complex

The results are given in Table 1.

Results and Discussions

A large number of complexes have been reported for the interactions of quinone with amino acids[7,8]. Sur[9] studied the donor-acceptor complexes of *p*-benzoquinone with amino acids (glycine, alanine, aspartic acid and glutamine) and inferred from the stability constant measurements (assuming 1 : 1 complex) that the strength of the donors is in the order glycine>glutamine>alanine>aspartic acid.

However, the colour development is not instantaneous and the complete complex formation requires

TABLE—1

Complexes	λ_{max}	ε_2	ε_1	K
1. PBQ : Glycine	495 nm	270	16.5	$9.4(\pm0.3)\times10^4$
2. PBQ : DL-α-Alanine	485 nm	400	19	$6.5(\pm0.2)\times10^4$
3. PBQ : γ-Amino Butyric acid	-	302.5 (λ=490 nm)	18	$1.7(\pm0.1)\times10^4$
4. PBQ : Methiontine	495 nm	504	16.8	$2.3(\pm0.1)\times10^5$
5. PBQ : L-Glutamine	490 nm	453	18	$7.6(\pm0.4)\times10^5$
6. PBQ : Tyrosine	-	305 (λ=490 nm)	18	$1.9(\pm0.3)\times10^4$
7. PBQ : Histidine	-	1800 (λ=500 nm)	15	$5.1(\pm0.3)\times10^5$
8. PBQ : Valin	497 nm	480	16	$3.8(\pm0.2)\times10^4$
9. PBQ : Proline	515 nm	930	10	$1.2(\pm0.1)\times10^5$
10. PBQ : Arginine	555 nm	1431.5	-	$6.2(\pm0.2)\times10^2$

The equilibrium constant had also been verified from measurements at different wavelengths.

appreciably long time indicating molecular complex formation or chemical reaction rather than charge transfer complex contrary to the observation by Sur.

Slifkin and co-workers[7,10,11] studied the C.T. complexes of amino acids with chloranil in aqueous ethanol with peaks at Ca 295 nm. A slowly developing pH-dependent new peak appeared (9 hr at pH 9, 24 hr at pH7 and 3 days at pH 4) at longer wavelengths between Ca 350 nm and 390 nm.

The rate of growth of the peak have been ascribed to the rate scheme

$$D + A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} (D:A)$$

The pH—dependence and the slow rate of the formation of complexes have been explained on the basis of conversion of Zwitter ion form (Z) to Neutral form (N) according to the equilibria $Z \rightleftharpoons N$ as the reaction proceeds and the pH increases.

The new peaks whose position change with pH have been ascribed to intrinsic band of chloranil shifted on complexing to that of the negative ion at 426 nm due to contribution of ionic structures to the structure of the complexed ion[11].

But it is not clear 1) Why the peak of the complexes should change so much ?

2) Why K_{form} should change with pH and wavelength ?

3) Why no account has been taken to the change in chloranil concentration due to its conversion to ionic form in calculating K and ϵ from Benesi—Hildebrand equation ?

Our studies reveal some important aspects. These are :

1) The marked increase in colour indicating the retention of quininoid structure.

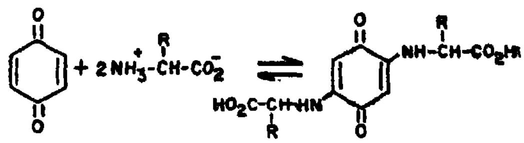
2) The relatively rapid effervescence of CO_2 when Na_2CO_3 was added to the solutions of the complexes than when added to amino acids alone.

3) The increase in conductivity of the solution of complexes is due to the presence of two carboxyl groups. Amino acids being 'Zwitter ions' are less conducting.

4) The compounds formed are highly soluble in water.

These facts lead us to suggest the following reaction schemes similar to that reported by Foster[6], Woker

a)

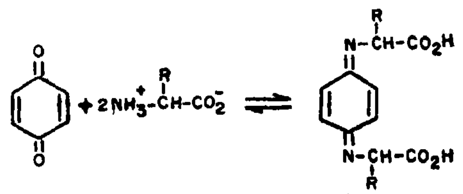


(X)

and Antener[12], Loffe and Khavin[13], Michalek and Szarkowska[14]. This type of additions to quinone is quite familiar particularly in case of thiol compounds which is supposed to occur in a number of biochemical processes i.e., in the antibacterial activity of quinone[15,16].

or

b)



(Y)

This may proceed via intermediate hydroquinone formation.

The fact that the compounds formed are highly soluble in water (more than amino acids) and less soluble in alcohol or other organic solvents leads us to believe that except for proline complexes of quinone, other compounds are of the type (Y). But we are not absolutely sure regarding the structures.

Absorption maxima are almost the same in all the cases indicating that almost all the compounds are of similar type. The stability constants of these compounds are also of the same order of magnitude as expected. The value of the stability constant decreases with branching but increases slightly with increasing chain length.

The 1 : 1 compound formation of tyrosine may be due to the involvement of OH-group as well as NH_2 group of the amino acid. The steric factor may be responsible for 1 : 1 compound formation in arginine. This amino acid is strongly basic due to its guanidino group and the stability, therefore, decreases as the amino acids are known to be good electron donors in acidic solution—a fact which is responsible for the change in K values in chloranil amino acid complexes[10]. The large bathochromic shift in arginine amino acid compound indicates greater conjugation.

One of the notable features is that the reactions are exergonic in character ($\Delta G = -6$ to -7 K. cals/mole in most cases) and can therefore, be utilised by suitable coupling mechanism to drive endergonic processes for analolizing complex biochemical substances.

Acknowledgement

The authors are thankful to C.S.I.R., Government of India, for a Research Fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 709-714

Fluctuation Theory and Microscopic Reversibility vis-a-vis Higher Order Symmetries†

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Manuscript received 27 June 1979, revised 19 March 1980, accepted 9 April 1980

Attempts have been made for obtaining higher order symmetries on the basis of the fluctuation theory and the theory of microscopic reversibility. The results obtained are in comformity with those obtained from steady state thermodynamic considerations.

THE basic foundation of the Onsager's reciprocity relation[1,2], which has, by now, very much stood the test[3-9] of time and is now accepted as an axiom is the fluctuation theory. The Li's higher order symmetries[10-11] which may be regarded as a logical extension or a mathematical corollary of the first order symmetry, still very much lie on the test board for a verdict on its merit, and only the future can give an assessment on this. An attempt to realize these higher order symmetries[10-18] in the perspect of the fluctuation theory[19-22] and the theory of microscopic reversibility[23-25] may be a useful contribution in this regard. The present communication is one such attempt in the said direction.

We consider an adiabatically insulated system defined or characterized by n degrees of advancement $\xi_1, \xi_2, \xi_3 \ldots \xi_n$ where n may become eventually infinite. The deviations of the ξ_i from their equilibrium value ξ^e_i is denoted by α_i so that

$$\alpha_i = (\xi_i - \xi^e_i) \quad \ldots \quad (1)$$

As state veriables we might think of local temperature, pressure, densities and the like for the description of the thermodynamical state of the system. The stress lies, in particular, on the point that in every microscopic theory one may choose continually varying parameters such as above, since in such cases only the number of variables become infinite. In the present discussion, however, we would like to advance our argument by using the degree of advancement from the equilibrium value as parameters.

The entropy change in any system is described by the sum total of the product of the fluxes, J_i, and their conjugate forces, X_i, operative in the system. If we choose A/T as a force, where A is the affinity of a chemical reaction at the temperature T of the system in Kelvin scale, then in present case of continuous range of advancement from equilibrium value, as the parameters, we obtain the entropy as given under

$$\Delta_i S = \int_{\xi^e}^{\xi} d_i S = \int_{\xi^e}^{\xi} \frac{A}{T} d\xi \quad \ldots \quad (2)$$

where $d\xi$ represents an infinitesinal change between the two subsequent advancements, which acts as a flux. Expressing A in the Taylor type expansion form, and remembering that A (ξ^e) i.e., equilibrium affinity of a chemical reaction, is zero[26], we rewrite equation (2) through equation (3) as given in equation (4)

$$A = \left(\frac{\delta A}{\delta \xi}\right)_o \alpha + \frac{1}{2!}\left(\frac{\delta^2 A}{\delta \xi^2}\right)_o \alpha^2 + \quad \ldots \quad (3)$$

$$\begin{aligned}\Delta_i S &= \int \left(\frac{A}{T}\right) d\xi \\ &= \frac{1}{T}\int \left[\left(\frac{\delta A}{\delta \xi}\right)_o \alpha + \frac{1}{2!}\left(\frac{\delta^2 A}{\delta \xi^2}\right)_o \alpha^2 + \ldots\right] d\xi \\ &= \frac{1}{T}\left(\frac{\delta A}{\delta \xi}\right)_o \frac{\alpha^2}{2} + \frac{1}{2!}\,\frac{1}{T}\left(\frac{\delta^2 A}{\delta \xi^2}\right)_o \frac{\alpha^3}{3} \\ &\quad + \ldots \quad (4)\end{aligned}$$

$\Delta_i S$, in equation (4) is the total entropy production occurring in the system which is thus obtained as the sum of the separate entropy contributions due to the various orders of deviations from equilibrium values of the different parameters which represent the various orders of forces operative in the system. These may be assumed to represent correspondingly the entropy contributions due to the first, the second and the third order forces etc., operating in the system and may be represented as

$$\Delta_i S = \Delta_i S' + \Delta_i S'' + \Delta_i S''' + \quad \ldots \quad (5)$$

†The paper, numbered Phy—53, was presented at the Annual Convention of Chemists 1979 held at Kurukshetra from 23 to 27 Sept. 1979.

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Differentiation of equation (4) with respect to α gives

$$\frac{\delta \Delta_i S}{\delta \alpha} = \frac{1}{T}\left(\frac{\delta A}{\delta \xi}\right)_o \alpha + \frac{1}{T}\frac{1}{2!}\left(\frac{\delta^2 A}{\delta \xi^2}\right)_o \alpha^2 + \ldots \quad (6)$$

which in the event of simultaneous fluctuations of various parameters of the system, takes a more general and comprehensive form as given under

$$\Delta_i S = \frac{1}{T}\frac{1}{2!}\sum_{ij}\left(\frac{\delta A_i}{\delta \xi_j}\right)_o \alpha_i \alpha_j + \frac{1}{T}\frac{1}{3!}\sum_{ijk}\left(\frac{\delta^2 A_i}{\delta \xi_j \delta \xi_k}\right)_o \alpha_i \alpha_j \alpha_k + \ldots \quad (7)$$

where i, j, k etc may each assume the values, 1,2,3, ...n. Equation (7) on differentiation with respect to α_i gives

$$\frac{\delta \Delta_i S}{\delta \alpha_i} = \frac{1}{T}\sum_j \left(\frac{\delta A_i}{\delta \xi_i}\right)_o \alpha_j + \frac{1}{T}\frac{1}{2!}\sum_{jk}\left(\frac{\delta^2 A_i}{\delta \xi_j \delta \xi_k}\right)_o \alpha_j \alpha_k \quad \ldots \quad (8)$$

Identifiying $\frac{1}{T}\left(\frac{\delta A}{\delta \xi_j}\right)_o$ with $-g_{ij}$ and

$\frac{1}{T}\left(\frac{\delta^2 A_i}{\delta \xi_j \delta \xi_k}\right)_o$ with $-g_{ijk}$ and so on equation (8) is written as

$$\frac{\delta \Delta_i S}{\delta \alpha_i} = -\sum_j g_{ijk}\, \alpha_j\, \alpha_k - \frac{1}{2!}\sum_{jk} g_{ijk}\, \alpha_i\, \alpha_k - \quad \ldots \quad (9)$$

Equation (5) on similar differentiation yields

$$\frac{\delta \Delta_i S}{\delta \alpha_i} = \frac{\delta \Delta_i S'}{\delta \alpha_i} + \frac{\delta \Delta_i S''}{\delta \alpha_i} + \frac{\delta \Delta_i S'''}{\delta \alpha_i} + \ldots = X_{ii} + X''_i + X'''_i + \ldots \quad (10)$$

where each of the terms in the r.h.s. of equation (10) is defined as the first, the second and the third order force etc and is correspondingly represented as $X'_i + X''_i + X''_i$ ... etc.

Equation (9) and (10) together give the following equalities

$$X'_i = \frac{\delta \Delta_i S'}{\delta \alpha_i} = -\sum_j g_{ij}\, \alpha_j$$

$$X''_i = \frac{\delta \Delta_i S''}{\delta \alpha_i} = -\frac{1}{2!}\sum_{jk} g_{ijk}\, \alpha_j\, \alpha_k$$

$$X'''_i = \frac{\delta \Delta_i S'''}{\delta \alpha_i} = -\frac{1}{3!}\sum_{jkl} g_{ijkl}\, \alpha_j\, \alpha_k\, \alpha_l$$

and so on ... (11)

Einstein's fluctuation theory[19-21] states that the probability of finding a state, in which the values of the α_i lie between α_i and $d\alpha_i$, is given[8,9] by

$$P d\alpha_1 d\alpha_2 \ldots d\alpha_n = \frac{e^{\Delta_i S/k}\, d\alpha_1\, d\alpha_2 \ldots\ldots d\alpha_n}{\int \ldots\ldots \int e^{\Delta_i S/k}\, d\alpha_1 d\alpha_2 \ldots d\alpha_n} \quad \ldots (12)$$

where the denominator on the right hand ensures normalisation of P over the complete configurational space to unity, i.e.,

$$\int \ldots \int e^{\Delta_i S/k}\, d\alpha_1 d\alpha_2 \ldots d\alpha_n = \int \ldots\ldots \int P d\alpha_1\, d\alpha_2 \ldots d\alpha_n = 1 \quad \ldots \quad (13)$$

where k in the above equations symbolises Boltzmann's constant.

Hence, from equations (12) and (5) we have,

$$P = e^{\Delta_i S/k} = e^{\Delta_i S'/k + \Delta_i S''/k + \Delta_i S'''/k + \ldots\ldots} = e^{\Delta_i S'/k} \cdot e^{\Delta_i S''/k} \cdot e^{\Delta_i S'''/k'''} \ldots\ldots \quad (14)$$

or

$$P = P'.P''.P'' \ldots\ldots \quad \ldots \quad (15)$$

where P is the total probability and P', P'' and P''' etc are the probabilities correspondingly related to $\Delta_i S'$, $\Delta_i S''$ and $\Delta_i S'''$ etc, which in turn are respectively connected with the first, the second and the third order forces etc. From equations (10), (14) and (15) we obtain

$$X_i' + X_i'' + X_i''' + \ldots = \frac{\delta \Delta_i S'}{\delta \alpha_i} + \frac{\delta \Delta_i S'}{\delta \alpha_i} + \frac{\delta \Delta_i S'''}{\delta \alpha_i} + \ldots$$

$$= \frac{K \delta \log P'''}{\delta \alpha_i} + \frac{K \delta \log P''}{\delta \alpha_i} + \frac{K \delta \log P''}{\delta \alpha_i} + \ldots (16)$$

Multiplication of the first, the second and the

third terms of the l. h. s. of equation (16) respectively by α_j, $\alpha_j \alpha_k$ and $\alpha_j \alpha_k \alpha_l$ etc and their averaging with the implication of equation (13), for normalisation condition, yields

$$\overline{X'_i\alpha_j}+\overline{X''_i\alpha_j\alpha_k}+\overline{X_i'''\alpha_j\alpha_k\alpha_l}+\ldots\ldots$$

$$=\int\ldots\ldots\int X'_i\,\alpha_j\,P'\,d\alpha_1.\,d\alpha_2\,\ldots\ldots d\alpha_n$$

$$+\int\ldots\ldots\int X'_i\alpha_j\alpha_k\,P''\,d\alpha_1\,d\alpha_2\ldots\ldots d\alpha_n$$

$$+\int\ldots\ldots\int X'''_i\alpha_j\,\alpha_k\alpha_l.\,P'''.\,d\alpha_1.\,d\alpha_2\,\ldots d\alpha_n$$

$$+\int\ldots\ldots\int\ldots\ldots \qquad\ldots\qquad (17)$$

Equation (17) in view of equation (16) may be read as

$$\overline{X'_i\,\alpha_j}+\overline{X''_i\,\alpha_j\,\alpha_k}+\overline{X'''_i\,\alpha_j\,\alpha_k\,\alpha_l}+\ldots\ldots$$

$$=K\int\ldots\ldots\int\alpha_j\,\frac{\delta\log P'}{\delta\,\alpha_i}P'\,d\alpha_1\,d\alpha_2\ldots d\alpha_n$$

$$+K\int\ldots\ldots\int\alpha_j\,\alpha_k\,\frac{\delta\log P''}{\delta\,\alpha_i}P''d\alpha_1 d\alpha_2\ldots d\alpha_n$$

$$+K\int\ldots\ldots\int\alpha_j\alpha_k\alpha_l\frac{\delta\log P'''}{\delta\alpha_i}P'''d\alpha_1 d\alpha_2\ldots d\alpha_n$$

$$+\;K\int\ldots\ldots\int\ldots\ldots \qquad\ldots\qquad (18)$$

Equating for the second terms of either sides of equation (18) leads to

$$\overline{X''_i\alpha_j\alpha_k}=K\int\ldots\ldots\int\alpha_j\,\alpha_k\,\frac{\delta\log P''}{\delta\,\alpha_i}P''.d\alpha_1\,d\alpha_2\ldots d\alpha_n \quad\ldots\;(19)$$

where X''_i is the second order force which includes the product of the two fluctuating parameters, of single order each, or the square of the fluctuation of the same parameter. We proceed with the more general condition by consididering two separate fluctuating parameters.

In the event of the fact that the resultant effect X'_i is given by two single fluctuating parameters such as X'_{i1} and X''_{i2} viz.

$$X''_i=X''_{i1}\,X''_{i2} \qquad\ldots\qquad (20)$$

so that we may split the average in the l. h. s. of equation (19) as given under

$$\overline{X''_i\,\alpha_j\,\alpha_k}=\overline{X''_{i1}\,\alpha_j}\;\overline{X''_{i2}\alpha_k} \qquad\ldots\;(21)$$

we, on the basis of the equation (18), obtain equation (22) from equation (21)

$$K\int\ldots\ldots\int\alpha_j\alpha_k\frac{\delta\log P''}{\delta\alpha_i}P''.\,d\alpha_1\,d\alpha_2\,\ldots\ldots d\alpha_n$$

$$=\left[K\int\ldots\ldots\int\alpha_j\;\frac{\delta\log P''_1}{\delta\alpha_i}P''_1.\,d\alpha_1.\,d\alpha_2\ldots d\alpha_n\right]$$

$$\left[K\int\ldots\ldots\int\alpha_k\,\frac{\delta\log P''_2}{\delta\alpha_i}P''_2.\,d\alpha_1.\,d\alpha_2\ldots d\alpha_n\right]\ldots(22)$$

where

$$X''_{i1}=\frac{K\,\delta\log P''_1}{\delta\alpha_i}$$

and

$$X''_{i2}=\frac{K\,\delta\log P''_2}{\delta\alpha_i}$$

Equation (22) is now written as

$$K\int\ldots\ldots\int\alpha_j\;\alpha_k\frac{\delta\log P''}{\delta\alpha_i}P''.\,d\alpha_1.\,d\alpha_2.\,\ldots d\alpha_n$$

$$=\left[K\int\ldots\ldots\int d\alpha_1 d\alpha_2\ldots\ldots d\alpha_{i-1}.\,d\alpha_{i+1}\ldots\ldots d\alpha_n\int\alpha_j\;\frac{\delta\log P''_1}{\delta\alpha_i}.\;P''_1\,d\alpha_i\right]$$

$$\left[K\int\ldots\ldots\int d\alpha_1\;d\alpha_2\ldots d\alpha_{i-1}.\,d\alpha_{i+1}\ldots d\alpha_n\int\alpha_k\,\frac{\delta\log P''_2}{\delta\alpha_i}P''_2.\,d\alpha_i\right]$$

$$=\left[K\int\ldots\ldots\int d\alpha_1.\,d\alpha_2\ldots\ldots d\alpha_{i-1}.\,d\alpha_{i+1}\ldots\ldots d\alpha_n\int\alpha_j\,\frac{1}{P''_1}\;\frac{\delta P''_1}{\delta\alpha_i}P''_1.\,d\alpha_i\right]$$

$$\left[K\int\ldots\ldots\int d\alpha_1\;d\alpha_2\ldots\ldots d\alpha_{i-1}.\,d\alpha_{i+1}\ldots\ldots d\alpha_n\int\alpha_k\frac{1}{P''_2}\;\frac{\delta P''_2}{\delta\alpha_i}P''_2\,d\alpha_i\right] \quad\ldots\quad (23)$$

Integration by parts of the r.h.s. of equation (23) yields

$$\left[K\int\ldots\ldots\ldots\int d\alpha_1.\,d\alpha_2\ldots.d\alpha_{i-1}.\,d\alpha_{i+1}\ldots\ldots d\alpha_n\right.$$

$$\left\{\left[\alpha_j P''_1\right]_{-\infty}^{+\infty}-\int_{-\infty}^{\infty}P''_1\frac{\delta\alpha_j}{\delta\alpha_i}d\alpha_i\right\}\Big]$$

$$\left[K \int \ldots\ldots\ldots \int d\alpha_1 . d\alpha_2 \ldots\ldots d\alpha_{i-1}\ d\alpha_{i+1} \ldots\ldots d\alpha_n .\right.$$

$$\left.\left\{\left[\alpha_k . P''_2\right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} P''_2\ \frac{\delta\alpha_k}{\delta\alpha_i}\ d\alpha_i \right\}\right] \ldots (24)$$

with the conditions that

P''_1 is zero for $\alpha_j = \pm\infty$ and

P''_2 is zero for $\alpha_k = \pm\infty$
expression (24) reduces to

$$\left[-K \int \ldots\ldots\ldots \int d\alpha_1 . d\alpha_2 \ldots d\alpha_{i-1} . d\alpha_{i+1} \ldots d\alpha_n \int P''_1 . \frac{\delta\alpha_j}{\delta\alpha_i} . d\alpha_i\right]$$

$$\left[-K \int \ldots\ldots\ldots \int d\alpha_1 . d\alpha_2 \ldots\ldots d\alpha_{i-1} . d\alpha_{i+1} \ldots d\alpha_n \int P''_2 . \frac{\delta\alpha_k}{\delta\alpha_i}\ d\alpha_i\right] \ldots (25)$$

Since α_i, α_j and α_k are independent variables, hence,

$\frac{\delta\alpha_j}{\delta\alpha_i} = 1$ or $\delta_{ij} = 1$ when $\alpha_i = \alpha_j$ and

$\frac{\delta\alpha_j}{\delta\alpha_i} = 0$ or $\delta_{ij} = 0$ when $\alpha_i \neq \alpha_j$

where δ_{ij} is the Kronecker symbol[9].

Similarly,

$\frac{\delta\alpha_k}{\delta\alpha_i} = 1$ or $\delta_{ik} = 1$ when $\alpha_i = \alpha_k$ and

$\frac{\delta\alpha_k}{\delta\alpha_i} = 0$ or $\delta_{ik} = 0$ when $\alpha_i = \alpha_k$

Expression (25) again reduces to

$$[-K \int \ldots\ldots \int d\alpha_1 .\ d\alpha_2 \ldots d\alpha_{i-1} .\ d\alpha_{i+1} \ldots d\alpha_n \int P''_1\ \delta_{ij} .\ d\alpha_i].$$

$$[-K \int \ldots\ldots \int d\alpha_1 .\ d\alpha_2 \ldots\ d\alpha_{i-1} .\ d\alpha_{i+1} \ldots d\alpha_n \int P''_2 \delta_{ik} d\alpha_i] \ \ldots (26)$$

using the normalisation condition, expression (26) gives,

$$[-K.\ \delta_{ij}]\ [-K.\ \delta_{ik}] = K^2.\ \delta_{ij}\ \delta_{ik} \qquad \ldots \quad (27)$$

The principle of microscopic reversibility[8,9,23-25] states that the correlation in an "aged" system among the values of α_h, α_i at a time instant t and a value of α_j a time τ later is the same as the correlation between $\alpha_h(t)$ $\alpha_i(t)$ and a value of α_j a time τ earlier[8,9]. The same fact may also be expressed in an alternative manner such as

$$\overline{\alpha_h(t)\ \alpha_i(t)\ \alpha_j(t+\tau)} = \overline{\alpha_h(t)\ \alpha_i(t+\tau)\ \alpha_j(t)} \qquad \ldots (28)$$

The averaging is performed by taking first, the fixed values of the parameters at the time t and then averaging the quantities belonging to the time $t+\tau$ followed by the application of the same consideration with all the parameters in question, and then finally averaging over all, which is expressed in the formula as

$$\overline{\alpha_h(t)\ \alpha_i(t)\ \overline{\{\alpha_j(t+\tau)\}}^{\alpha_h(t)\ \ldots\ \alpha_n(t)}}$$

$$= \overline{\alpha_h(t)\ \alpha_j(t)\ \overline{\{\alpha_i(t+\tau)\}}^{\alpha_h(t)\ \ldots\ \alpha_n(t)}} \qquad \ldots \quad (29)$$

following the procedure of De Groot[9], and subtracting the same quantity, $\alpha_h(t)\ \alpha_i(t)\ \alpha_j(t)$ from both members of equation(29) we obtain

$$\overline{\alpha_h(t)\ \alpha_i(t) \overline{\{\alpha_j(t+\tau) - \alpha_j(t)\}}^{\alpha_h(t)\ \ldots\ \alpha_n(t)}}$$

$$= \overline{\alpha_h(t)\ \alpha_j(t) \overline{\{\alpha_i(t+\tau) - \alpha_i(t)\}}^{\alpha_h(t)\ \ldots\ \alpha_n(t)}} \ \ldots \ (30)$$

we now co-relate the rate of decay as linear combination with the second order force (X''_k), [c. f. equation (10)] as follows

$$\frac{\overline{\alpha_i(t+\tau) - \alpha_i(t)}}{\tau} = \dot{\bar{\alpha}}.\ \text{(rate of decay)}$$

$$= J_i\ \text{(flux)}$$

$$= \sum_{h,k=1}^{n} L_{ihk}\, X''_k \qquad \ldots \qquad (31)$$

the l. h. s. of equation (31) denote the rate of decay of fluctuation and L_{ihk} in the r. h. s. is the second order phenomenological coefficient of the second order force of the type X''_k. In equation (31) the time interval τ is limited by the conditions[9]

$$\tau_0 << \tau << \tau_r$$

where τ_0 is the characteristic molecular time i.e., the time between two successive collisions of the molecules and τ_r is the regression time of a fluctuation i.e., at a time in which the deviation from equilibrium is appreciably reduced. On similar consideration we obtain

$$\frac{\overline{\alpha_j(t+\tau) - \alpha_j(t)}}{\tau} = \dot{\bar{\alpha}}_j \equiv J_j = \sum_{h,k=1}^{n} L_{jhk}\, X''_k \qquad \ldots \quad (32)$$

On the basis of equations (31) and (32) one gets from equation (30) as

$$\overline{\dot{\bar{\alpha}}_j(t)\ \alpha_i(t)\ \alpha_h(t)} = \overline{\dot{\bar{\alpha}}_i(t)\ \alpha_j(t)\ \alpha_h(t)} \ \ldots \qquad (33)$$

Putting the value of equations (31) and (32) in equation (33) we have

$$\sum_{h,k} L_{ihk} \cdot \overline{\alpha_j \, \alpha_h \, X_k''} = \sum_{h,k} L_{jhk} \, \overline{\alpha_i \, \alpha_h X_k''} \quad \ldots \quad (34)$$

Equations (33) and (34) read with equation (27) give

$$\overline{\alpha_j \, \alpha_h X_k''} = K^2 \, [\,\delta_{kj} . \, \delta_{kh}] \quad \ldots \quad (35)$$

and

$$\overline{\alpha_i \, \alpha_h \, X_k''} = k^2 [\delta_{ki} \cdot \delta_{kh}] \quad \ldots \quad (36)$$

Putting the value of equations (33) and (36) in equation (34) we obtain

$$K^2 \sum_{h,k} \left[\;\delta_{kj} . \, \delta_{kh} \;\right] L_{ihk} = K^2 \sum_{h,k} [\,\delta_{ki} . \, \delta_{kh}] \, L_{jhk}$$

or

$$\sum_{h\,k} [\,\delta_{kj} . \, \delta_{kh} \;] \, L_{ihk} = \sum_{h,k} [\,\delta_{ki} . \, \delta_{kh}] \, L_{jhk} \quad \ldots \quad (37)$$

Kronecker symbols δ_{kj}, δ_{kh} and δ_{ki} come out unity in the l.h.s. and r.h.s. of equation (37) when

$$K = j, \qquad \delta_{kj} = \delta_{,,} = 1$$

$$K = h, \qquad \delta_{kh} = \delta_{,,} = 1$$

$$K = i, \qquad \delta_{ki} = \delta_{,,} = 1 \quad \ldots \quad (38)$$

Equation (37) is valid only for the conditions expressed in (38). Putting the condition of equation (38) in equation (37) we obtain the second order symmetries as given under

$$\sum L_{ihk} = \sum L_{jhk} \quad \ldots \quad (39)$$

To examplify the validity of the equality expressed above we consider first the l.h.s. of equation (39) with the condition given in the r.h.s. of equation (40). This yields

and then the r.h.s. of equation (39) with the condition mentioned in the r.h.s. of equation (41), which yields

$$\sum L_{ihk} = \sum^{j=h=k} L_{ijj} \quad \ldots \quad (40)$$

$$\sum L_{jhk} = \sum^{j=h,\; i=k} L_{jji} \quad \ldots \quad (41)$$

whereby we obtain

$$\sum^{j=h=k} L_{ijj} \;' = \sum^{j=h,\; i=k} L_{jji} \quad \ldots \quad (42)$$

and similarly we also obtain,

$$\sum^{i=h,\; j=k} L_{iij} = \sum^{i=h=k} L_{jii} \quad \ldots \quad (43)$$

Likewise if we proceed with third term of the expression (18) and utilising the same procedure as adopted earlier we get

$$\overline{X_i''' \, \alpha_j \alpha_k \alpha_l} = K \int \ldots\ldots\ldots \int \alpha_j \alpha_k \alpha_l \, \frac{\delta \log p''}{\delta \alpha_i} \, p''. d\alpha_1 . d\alpha_2 \; \ldots\ldots\ldots \; d\alpha_n .$$

Splitting X_i''' as the product of three fluctuating parameters i.e.,

$$X_i''' = \hat{X}_{i1}''' \; \hat{X}_{i2}''' \; \hat{X}_{i3}'' \quad \ldots \quad (44)$$

and stepping on the footsteps of our previous arguments (c.f. equation 21-27) we obtain,

$$\overline{X_i''' \, , \alpha_j \alpha_k \alpha_l} = \overline{\hat{X}_{i1}''' \alpha_j} . \overline{\hat{X}_{i2}''' \alpha_k} \overline{\hat{X}_{i3}'' \alpha_l}$$

$$= -K^3 [\delta_{ij} . \, \delta_{ik} . \, \delta_{il} \,] \quad \ldots \quad (45)$$

which finally gives,

$$-K^3 \sum_{hkl} \left[\, \delta_{kj} . \, \delta_{kh} . \, \delta_{kl} \; \right] L_{ihkl}$$

$$= -K^3 \sum_{hkl} \left[\, \delta_{ki} . \, \delta_{kh} . \, \delta_{kl} \; \right] L_{jhkl} \quad \ldots \quad (46)$$

and from this we obtain, the third order symmetries of the form,

$$\sum L_{ihkl} = \sum L_{jhkl} \quad \ldots \quad (47)$$

The equality given in (47) may similarly be tested. This, with the condition mentioned under, gives the symmetries of the type

$$\sum^{j=k=l,\; i=h} L_{ijjj} = \sum^{i=h=l,\; j=h} L_{jii} \quad \ldots \quad (48)$$

$$\sum^{j=h=k=l} L_{ijjj} = \sum^{j=h=k,\; i=l} L_{jjji} \quad \ldots \quad (49)$$

and

$$\sum^{i=j=k,\ j=l} L_{iiij} = \sum^{i=h=k=l} L_{jiii} \qquad \dots \quad (50)$$

From what have been discussed above it would be evidently clear that if we proceed with the force of fourth and fifth terms etc of equation (18) respectively with identical approach we would correspondingly observe the fourth and fifth order symmetries etc. as has been verified on kinetic considerations of the classical theories in some of the earlier communications[14,16,27], as a logical consequence.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 715-719

Thermodynamics of Bromoform and Ethanol Mixtures

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Manuscript received 25 May 1979, revised 6 February 1980, accepted 31 March 1980

Heats of mixing and vapour pressures of bromoform (A)+ethanol (B) as a function of concentration have been determined at 303.15 K. The excess Gibbsn free energy of mixing, G^E values have been obtained from the measured vapour pressure data. The heats of mixing, H^E and G^E values are positive throughout the entire bromoform concentration range and $G^E > H^E$. The results have been analysed in terms of Barker and ideal associated model theory of non-electrolyte solutions. The analysis have revealed that both Barker theory and the ideal associated model approach [which here assumes the presence of A_mB (m = 1 2), AB_k (K = 2) and B_l (l = 1) molecular species] well describe the general behaviour of H^E with X_A over the entire bromoform concentration range for this mixture. The equilibrium constants for the various association reactions alongwith the enthalpy of formation of the various molecular species have also been calculated.

FOLLOWING Frank and Wen's model[1] of liquid water, it was believed that alcohols should also possess a similar type of cooperativity in the formation of hydrogen-bonded polymers. But there is considerable disagreement as to the identity of the predominant associated species[2-6]. Again while the solution hetero-associated data[7,8] have been limited to calculation of equilibrium constants for 1 : 1 and 2 : 1 complexes only, Tucker and Christian[9] have interpreted the results for their distribution studies to indicate that lower alkanols contain monomers, dimers and higher r-mers. The present work describes interactions in bromoform+ethanol mixtures.

Experimental

Materials and Methods :

Analytical grade ethanol (B.D.H) and bromoform (E. Merck A.R.) were purified in the manner suggested by Vogel[10]. The purity of the final samples was checked by density determinations at 298.15 ±0.01K which agreed to within 0.00005 g. ml^{-1} with the literature values[11,12].

Heats of mixing measurements at 303.15±0.01K were made in an adiabatic calorimeter described elsewhere[13]. The performance of the calorimeter was tested by determining the heats of mixing of benzene and cyclohexane at 298.15±0.01K and these agreed to within 0.3 percent (over the central range of concentration) with the corresponding literature values[14].

Vapour pressures of bromoform+ethanol mixtures were determined by a static method in the manner described previously[15]. All vapour pressure measurements were reproducible to better than ±0.02 torr.

The measured vapour pressure (78.12 torr) of ethanol at 303.15K agreed within 0.1 per cent with that (78.30 torr) at 303.15K obtained by Ferguson *et al*[16]. We are unaware of any vapour pressure data at 303.15K with which to compare our measured vapour pressure of bromoform.

Results

The molar heats of mixing H^E, and the measured vapour pressure data at 303.15K for bromoform+ethanol are recorded in Tables 1 and 2 respectively. The H^E,G^E and TS^E data are plotted in Figs. 1 and 2.

The H^E data (Table 1) were fitted to the expression

$$\frac{H^E}{X_A(1-X_A)} = [h_0 + h_1(2x_A - 1) + h_2(2x_A - 1)^2] \quad ... \quad (1)$$

where X_A is the mole fraction of bromoform. The parameters h_0, h_1 and h_2 evaluated by fitting

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TABLE 1 — MEASURED MOLAR HEATS OF MIXING FOR DIFFERENT MOLE FRACTIONS XA OF BROMOFORM AT 303.15 K

X_A	H^E/J mol^{-1}	X_A	H^E/J mol^{-1}
		Bromoform (A) + ethanol (B)	
0.1197	-43.08	0.5399	506 64
0.1501	-30.47	0.5801	558.71
0.2250	34.13	0.6353	611.58
0.2703	90.88	0.6850	639.75
0.3398	191.43	0.7503	634.99
0.4100	306.23	0.7852	610.47
0.4552	381.45	0.8201	568.29
0.4902	435.00	0.8950	413.35

TABLE 2 — MEASURED TOTAL VAPOUR PRESSURE, P; ACTIVITY COEFFICIENT, γ; RESIDUAL VAPOUR PRESSURE $R = P_{exptl} - P_{calc}$; MOLAR EXCESS GIBBS FREE ENERGIES, G^E; AND TS^E FOR DIFFERENT MOLE FRACTIONS XA OF BROMOFORM AT 303 15 K

X_A	P/Torr	γ_A	γ_B	P_A/Torr	P_B/Torr	$R = P_{exptl} - P_{calc}$	G^E/J mol^{-1}	TS^E/J mol^{-1}
				Bromoform(A) + ethanol (B)				
0.0000	78 21	3.5589	1.0000	0.00	78.21	0.00	0.00	0.00
0.0903	73.99	2.8552	1.0088	2.39	71 76	-0.16	261.96	-306.40
0.1502	71.56	2.5354	1.0241	3.53	68 04	-0.01	408.49	-436.68
0 2750	66.53	2 0684	1.0813	5.27	61.28	-0.02	651.77	-557.61
0.3697	63.17	1.8127	1.1530	6.21	56.80	0.15	782.83	-544.92
0.4503	60.15	1.6323	1 2419	6.80	53.35	-0.00	856.65	-486.20
0.5300	57.43	1.4773	1.3675	7.25	50 22	-0.04	892.22	-397.51
0.6601	53.17	1.2665	1.7138	7.73	45.51	-0.07	857 22	-226.91
0.7799	48.68	1.1201	2.3524	8.08	40.44	0.15	700.71	-83.09
0.8402	44.54	1.0660	2 9137	8.28	36.36	-0.10	567.60	-29.28
0.9250	33.67	1.0155	4 2664	8.67	24.97	0.01	308.46	10.21
1.0000	9.21	1.0000	6.5812	9.21	0.00	0.00	0.00	0.00

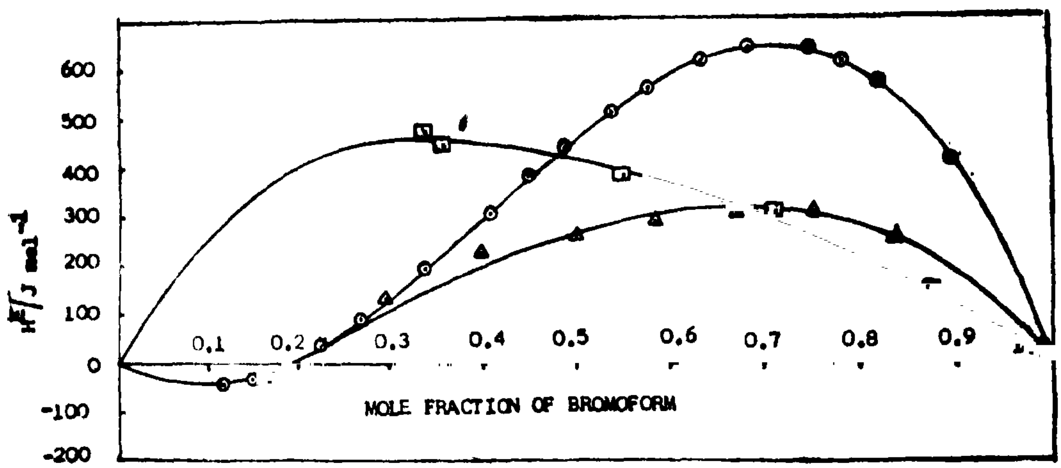


Fig. 1. Enthalpies of Mixing H^E for Bromoform(1) + Elhanol(2) at 303. 15 K, O, experimental H^E; △, calculated H^E according to ideal associated model that assumes the presence of AB, AB_2, A_2B and B molecular species ; ▭, calculated H^E according to ideal associated model that assumes the presence of AB, AB_2. AB_3 and B molecular species ($K_{1\cdot 0\cdot 5}$ = 0,09, ΔH_{AB} = −0.5 KJ mol^{-1} : $K_{0\cdot 5}$ = 0.04, ΔH_B = 2.5 KJ mol^{-1} ; $K_{1,1}$ = 0.7. ΔH_{AB_2} = −1.15 KJ mol^{-1} : $K_{1,2\cdot 5}$ = 0.06, ΔH_{AB_3} = −0.5 KJmo^{-1})

$H^E/x_A(1-x_A)$ to expression (1) by the method of least squares are given together with the standard deviation of the molar heats of mixing, $\sigma(H^E)$ in Table 3.

The vapour pressure data were used to evaluate the molar excess Gibbs free energy, G^E, by Barker's method[17]. The form of the function used for G^E, following Redlich Kister[18] as

$$G^E/RT = x_A(1-x_A)[G_0 + G_1(2x_A-1) + G_2(2x_A-1)^2 + G_3(2x_A-1)^3] \quad \ldots \quad (2)$$

where G_0, G_1, G_2 and G_3 are adjustable parameters.

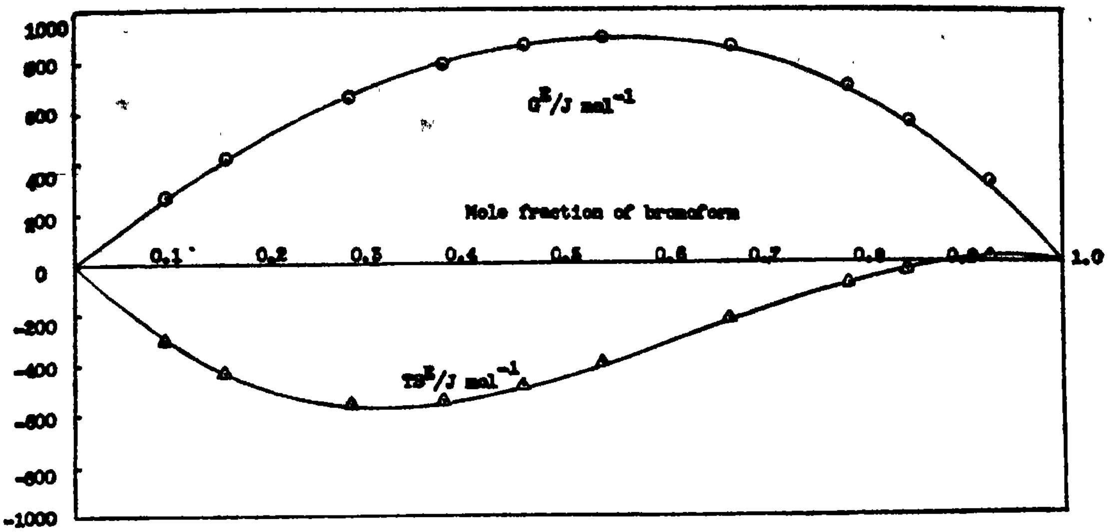


Fig. 2. Excess functions for bromoform (A) + ethanol (B) at 303.15 K ⊙, G^E ; and △, TS^E

These parameters are recorded in Table 3. The second virial coefficients of ethanol were evaluated from the Berthelot relation[19] using critical constant data[20,21]. The critical constants, V_c , P_c and T_c of bromoform were evaluated from the Lyderson method, the Riedel method and the modified Guldberg rule, respectively as reported[20]. The cross virial coefficients were taken as $(B_{11}+B_{22})/2$. The thermodynamic consistency of the data were tested[18] by plotting ln (γ_A / γ_B) versus x_A. The positive and negative areas bounded by the curve ln (γ_A / γ_B) versus x_A and the X-axis agreed to better than 0.2 percent.

curve of TS^E against $X_{ethanol}$ is highly unsymmetrical about $X_{ethanol}$.

At the simplest qualitative level the observed H^E data for this mixture may be accounted for if we assume that (i) ethanol is self-associated and there is a change (decrease) in its self-association when it is mixed with bromoform, (ii) there is a hydrogen-bonded interaction between the hydroxyl oxygen of ethanol and the bromoform hydrogen and (iii) there is specific interaction between the hydroxyl hydrogen of ethanol with the bromine of bromoform. The negative values of H^E for high ethanol concentrations are

TABLE 3 – PARAMETERS Xm (X = h OR G) OF EQUATIONS 1 AND 2, STANDARD DEVIATION OF PRESSURE σ(P) ALONGWITH THE STANDARD DEVIATION OF H^E, $\sigma(H^E)$ FOR BROMOFORM (A) + ETHANOL (B) MIXTURE AT 303.15 K

m	0	1	2	3	$\sigma(H^E)$/J mol^{-1}	σ(P)/Torr
h_m	1801.00	3067.84	255.79	-	2.38	-
G_m	1.4021	0.3073	0.1556	-0.0190	-	0.12

Discussion

We are unaware of any H^E or G^E data for bromoform+ethanol with which to compare our results.

Heats of mixing for bromoform (A)+ethanol (B) are negative for solution rich in ethanol but they become positive for solutions rich in bromoform. The S-shaped H^E curve attains a maximum negative value of 45 J mol^{-1} at $X_{ethanol}$ = 0.90 and maximum positive value of 640 J mol^{-1} at $X_{ethanol}$ = 0.29. Further TS^E is negative at all the ethanol mole fractions (except for $X_{ethanol}$ = 0.075) for which the experimental data are available and the

then due essentially to the factor (ii). This is because while interactions due to the factor(ii) can occur without breaking the alcohol-alcohol hydrogen bond, the same is not true of interactions due to factor(iii). Again in the hydrogen bonded interaction due to factor(ii) limits the orientational freedom of the bromoform molecules thus making TS^E strongly negative so that G^E should be (as indeed is) positive. The positive values of H^E at high bromoform concentrations are due to the rupture of alcohol-alcohol hydrogen bonds followed by their subsequent hydrogen-bonded interaction with bromoform molecules. This in turn would require the TS^E at high bromoform concentrations to be considerably more positive than that at low bromoform concentrations and thus explains

the unsymmetrical nature of TS^E versus $X_{bromoform}$ curve.

We examined our results using Barker's theory[22]. It was assumed that bromoform (A) and ethanol (B) have the following geometrical parameters:

Lattice $z = 4$
Bromoform molecules (A)
$r_A = 3\ Q_{R'}^{A} = 1\ Q_{R'}^{A} = 7$
Ethanol molecules (B)
$r_B = 2\ Q_O^B = 2\ Q_H^B = 1\ Q_R^B = 3$

where O, H and R respectively, hydroxyl oxygen, hydrogen and hydrocarbon surface of ethanol, and H' and R' represent the hydrogen and bromine surface of bromoform. The interactions first considered were a specific (O ..... H') interaction of strength U_3 between the hydroxyl oxygen of ethanol and the hydrogen of bromoform, a specific (O .....H) interaction of strength U_2 between the hydroxyl oxygen and hydroxyl hydrogen of ethanol and a non-specific interaction for all the remaining contact points. For the sake of simplicity these non-specific interactions for all the remaining contact points were considered to have the same strength U_1. Excess energy of mixing at constant volume U_V^E, values at $X_A = 0.3$, 0.5 and 0.7 were then calculated[22] from this theory and they did not reproduce the experimental H^E values. (It is customary while testing a lattice theory to convert U_V^E values to measurements at constant pressure, H^E, using the relation $U_V^E = H^E - TV^E\alpha_m/(K_T)_m$ where α_m, $(K_T)_m$ and V^E are respectively the expansivity, isothermal compressibility and excess volume of the mixture. However, since V^E is small (V^E for an equimolar mixture is -0.180 $cm^3\ mol^{-1}$), contribution of $TV^E\alpha_m/(K_T)_m$ term would be negligibly small and for the present analysis we have assumed $U_V^E \approx H^E$. The best values of U_1, U_2, U_3 (designated as $U_i^{(1)}$ ($i = 1$ to 3) and the corresponding H^E values designated as $H^{E(1)}$ are recorded in Table 4.

We next considered a slightly different model in which in addition to the above interaction, one of the bromines of bromoform was assumed to be involved in a specific (H.. Br) interaction of strength U_4 with the hydroxyl hydrogen of ethanol. The bromoform was considered to have the following $Q_{R'}^{A'} = 6$. The agreement between the theoretical[22] and the experimental H^E values is now better as compared to the earlier one although it still is by no means quantitative. (The values of of U_i ($i = 1$ to 4) and H^E are designated as $U_i^{(2)}$ and $H^{E(2)}$ in Table 4).

The interaction energies and the H^E and G^E values at $X_A = 0.3$, 0.5 and 0.7 calculated from this theory are recorded in Table 4, and they compare reasonably well with the corresponding experimental values. The theoretical results thus show similar qualitative behaviour to that shown by the experimental data. Models of bromoform molecules with two and three hydrogen contact points were also considered but they did not give better results. Perhaps associated complexes of the general formula A_1B_1 and B_n are present in these mixtures. H^E and G^E data for this mixture were then analysed in terms of the ideal associated model[23,24] which assumed that in a binary solution of bromoform (A) and ethanol (designated as B_n since ethanol is self-associated) mutual equilibrium of the species A_mB, AB_k and B_l ($l = 1,2,3... l$; $K = 1,2,3..... k$; $n = 1,2,3......n$; $m = 2,3..... m$) exist according to the reactions

$$mA + B_n \rightleftharpoons A_mB + AB_k + B_l \quad \dots (3)$$

so that the equilibrium constants for the various association reactions represented by equation (3) are

$$K_{m,\frac{1}{\bar{n}}} = a_{A_mB} \Big/ a_A^m\, a_{B_n}^{\frac{1}{\bar{n}}} \quad \dots (4)$$

$$K_{1\,k} = a_{AB_k} \Big/ a_A\, a_{B_n}^{k/n} \quad \dots (5)$$

and $$K_l/n = a_{B_l} \Big/ a_{B_n}^{l/n} \quad \dots (6)$$

TABLE 4—COMPARISON OF H^E AND G^E VALUES CALCULATED ACCORDING TO BARKER'S THEORY WITH VALUES NITERPOLATED FROM THE MEASURED VALUES AT THREE MOLE FRACTIONS OF THE COMPONENT (A) AND THE INTERACTION ENERGIES OF BROMOFORM (A)+ETHANOL (B) AT 303.15 K

Property/J mol⁻¹	The mole fraction of the component (A) 0.3	0.5	0.7	Interaction energies/J mol⁻¹
H^E_{exptl}	130.00	450.00	640.00	
$H^{E(1)}$	426.73	653.04	564.27	$U_1^{(1)} = 322.3$, $U_2^{(1)} = -2309.48$, $U_3^{(1)} = -1987.35$
$H^{E(2)}$	353.77	444.86	292.38	$U_1^{(2)} = 161.36$, $U_2^{(2)} = -2309.48$; $U_3^{(2)} = -1987.35$; $U_4^{(2)} = -1618.18$
G^E_{exptl}	690.00	882.00	810.00	
$G^{E(2)}$	400.75	455.35	531.70	

TABLE 5—THE EQUILIBRIUM CONSTANTS (MOLE FRACTION SCALE) FOR THE VARIOUS COMPLEXING REACTIONS TOGETHER WITH THE ENTHALPIES OF FORMATION OF VARIOUS MOLECULAR SPECIES AND THE VARIANCE OF THE FIT σD^2 AT 303.15 K

Equilibrium constants	Reaction of bromoform with ethanol	Parameter	Mixtures of ethanol(B) with bromoform (A)
$K_{1,0.5}$	0.10	ΔH_{AB}/KJ mol^{-1}	-0.50
$K_{2,0.5}$	0.05	ΔH_{A_2B}/KJ mol^{-1}	-0.50
$K_{1,1}$	0.80	ΔH_{AB_2}/KJ mol^{-1}	-1.15
$K_{0.5}$	0.04	ΔH_B /KJ mol^{-1}	2.50
		$\sigma D^2_{\gamma_0}$	0.016
		$\sigma D^2_{\gamma_1}$	0.019

where 'a' denotes activities in the manner described previously[25]. The analysis of the activity coefficient data suggests that these mixtures may be assumed to have either AB, A_2B, AB_2 and B or AB, AB_2, AB_3 and B molecular species in solution. We next considered our H^E data in the manner described earlier[25].

Examination of the H^E data of this mixture in terms of models that involved consideration of

i) AB, A_2B, AB_2 and B, and

ii) AB, AB_2, AB_3 and B molecular species.

Using the various K values for a solution containing AB, A_2B, AB_2 and B species, we obtained[25] the various ΔH values which are recorded in Table 5. The calculated H^E values are plotted in fig. 1. It is evident from this fig. that the theoretical H^E values well describe the general behaviour of H^E with X_A for bromoform (A) + ethanol (B_2) mixture.

A similar process was applied to the case when the mixture contain AB_m (m = 1 to 3) and B molecular species. However, no values of ΔH_{AB_m} (m = 1 to 3) and ΔH_B could yield H^E values that described the experimental behaviour of H^E with X_A for this mixture. The calculated H^E values are either positive or negative throughout the entire bromoform concentration range. Further the quantitative agreement is also not good. (See Fig. 1 where only those ΔH_{AB_m} and ΔH_B values are considered that render H^E_{cacl} positive throughout the entire bromoform concentration range).

The analysis of H^E and activity coefficient data for bromoform + ethanol mixture thus suggests that this mixture is characterized by the presence of AB, AB_2, A_2B and B molecular species in solution.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 720-721

On the Huggins Constants for Methyl Methacrylate-Acrylonitrile Random Copolymers

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Manuscript received 2 January 1979, revised 23 July 1979, accepted 31 March 1980

This paper considers random copolymers of methyl methacrylate with acrylonitrile. It describes an assessment of solvent power for polymers on the basis of the Huggins constant k', and a comparison is made with other criteria of solvent power.

IN an earlier study dealing with the effect of composition on the Huggins constant, k' for methyl methacrylate acrylonitrile random copolymers[1], it was concluded that the value of k' is dependent strongly both on the composition of the copolymer as well as the nature of the solvent. Whereas, the former study dealt with our preliminary viscosity experiments on unfractionated copolymers, the present study refers to detailed studies on the Huggins constant for fractionated copolymers. With the availability of the data on the various solution properties of these copolymers[2-5], viz., Mark-Houwink Exponent, a, copolymer-solvent interaction parameter χ_1, it is also intended to see whether k' could be considered as a measure of the solvent power for the copolymer systems.

Experimental

The copolymers were prepared by solution polymerization method and fractionated by fractional precipitation method. The details of preparation, criteria for selection of various solvent-nonsolvent pairs for fractionation etc. have been reported earlier[4]. The data on light scattering and viscosity measurements, and evaluation of various parameters, such as Mark-Houwink constants, short range and long range interaction parameters, have been reported elsewhere[2-5].

Results and Discussion

Huggins constant, is evaluated from the slope of $\frac{\eta_{sp}}{C}$ vs C. plots, in accordance with following equation :

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C$$

The values of k' were found for the copolymer fractions in methyl ethylketone (MEK), acetonitrile (MeCN), dimethyl formamide (DMF), γ-butyrolactone (γ-BL) at 30°, 45° and 60°, from the usual Huggins plots (See Tables 1-4). The data for the evaluation of k' were treated by the least square method[6].

TABLE 1 – HUGGINS CONSTANTS, FOR MA1 (COMPOSITION : 0.289 M.F. OF AN)

Fraction	$\bar{M}_w \times 10^{-5}$	MEK	MeCN	DMF			γ-BL		
		30°	30°	30°	45°	60°	30°	45°	60°
MA111	79.03	0.51	0.52	0.35	0.33	0.36	0.39	0.37	0.29
MA121	47.72	0.53	0.55	0.33	0.36	0.31	0.28	0.35	0.16
MA122	42.95	0.54	0.53	0.36	0.38	0.39	0.31	0.35	0.35
MA14	31.61	0.60	0.60	0.41	0.39	0.41	0.40	0.38	0.33
MA15	23.71	0.48	0.47	0.37	0.34	0.30	0.25	0.36	0.36
MA17	8.38	0.43	0.46	0.39	0.22	0 44	0.43	0.90	0.32

TABLE 2—HUGGINS CONSTANTS FOR MA2 (COMPOSITION : 0.415 M.F. OF AN)

Fraction	$\bar{M}_w \times 10^{-5}$	MEK	MeCN	DMF			γ-BL		
		30°	30°	30°	45°	60°	30°	45°	60°
MA211	25.12	0.82	0.52	0.12	0.17	0.19	0.45	0.38	0.40
MA24	9.30	0.58	0.45	0.11	0.08	0.05	0.42	0.54	0.35
MA212	9.18	0.76	0.60	0.05	0.31	0.34	0.53	0.48	0.46
MA25	6.33	0.57	0.50	-0.12	0.28	0.25	0.88	0.85	0.52
MA27	1.65	0.43	0.35	-0.31	0.30	-0.40	0.42	0.36	0.27

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TABLE 3—HUGGINS CONSTANTS FOR MA3 (COMPOSITION : 0.566 M.F. OF AN)*

Fraction	$\bar{M}_w \times 10^{-5}$	MEK	MeCN	DMF			γ-BL		
		30°	30°	30°	45°	60°	30°	45°	60°
MA311	12.95	0.51	0.45	0.48	0.46	0.43	0.34	0.39	0.44
MA321	9.99	0.67	0.53	0.38	0.43	0.23	0.31	0.31	0.29
MA33	6.99	0.71	0.52	0.58	0.53	0.49	0.25	0.32	0.37
MA34	6.30	0.82	0 60	0.34	0.38	0.36	0.22	0.26	0.21
MA35	5.01	0.63	0.48	0.36	0.40	0.29	0.38	0.38	0.36

TABLE 4—HUGGINS CONSTANTS, k' FOR MA4 (COMPOSITION : 0.657 M.F. OF AN)

Fraction	$\bar{M}_w \times 10^{-5}$	MeCN	DMF			γ-BL		
		30°	30°	45°	60°	30°	45°	60°
MA421	8.99	0.73	0.41	0.46	0.47	0.40	0.37	0.36
MA431	6.42	0.68	0.44	0.40	0.45	0.42	0.38	0.33
MA433	4.63	0.82	0.56	0.52	0.49	0.58	0.40	0.41
MA45	3.17	0.79	0.54	0.48	0.53	0.60	0.39	0 43
MA46	2.48	0.43	0.16	0.19	0.28	0.35	0.37	0.26

It is seen that k' depends on molecular weight, solvent and temperature for a particular composition of copolymer. The dependence of k' on the mol ecular weight is contrary to the observations made by Huggins[7], that k' is to be independent of molecular weight, in view of the fact that these copolymers were fractionated with respect to molecular weight alone[6]. For the copolymer fractions of similar molecular weight, the solvent power for various solvents has been classified, based on k' values (Table 5).

It is obvious that except for MA2, the solvent power for other copolymers is MEK<MeCN<DMF <γ-BL. The effect of composition on this order is not noticed. It is to be noted that, whereas MEK and MeCN are nonsolvents for one or both parent homopolymers, DMF & γ-BL are solvents for both the parent homopolymers. The effect of temperature on k' is not of a uniform nature.

From the present study, it follows that k' could be taken as a fairly accurate parameter for determining the solvent power of various solvents. The evaluation of k' is simple and does not involve the handling of delicate instruments such as Light Scattering Photometers or Osmometers.

TABLE 5—SOLVENT POWERS OF VARIOUS SOLVENTS, BASED ON THE PARAMETERS k', a, B AND χ_1 :

	MA1	MA2	MA3	MA4
k'	1<2<3<4	1<2<4<3	1<2<3<4	2<3<4
a	1<2<3<4	3<4<1<2	1<3<4<2	2<3<4
B	1<2<3<4	1<4<2<3	1<2<3<4	2<3<4
χ_1	2<1<3<4	2<1<4<3	2<1<3<4	2<3<4

1 = MEK ; 2 = MeCN ; 3 = DMF ; 4 = γ-BL.

Table 5 also includes the solvent power of the same set of solvents based on a, B and χ_1[2-5]. It is important to emphasize that, whereas B and χ_1 (related to B through molal volume of the solvent) are measures of long range interactions between polymer and solvent when the chain extension occurs through polymer-solvent interactions alone, k' and a depict the overall picture of the various kinds of interactions.

In our studies on the dilute solution properties of these copolymers[2-5], it was concluded that these copolymers assume large extension mainly due to short range interactions, rather than long range interactions. Further, it was also concluded that Stockmayer-Fixman equations or variants thereof may have to be modified for such polar systems. Therefore, it appears that B and χ_1 could be considered as of limited and qualitative significance only.

From Table 5, the solvent power of various solvents are as follows :

MEK ⩽ MeCN < DMF < γ-BL : MA1
MEK < MeCN ⩽ γ-BL < DMF : MA2
MEK < MeCN ⩽ DMF < γ-BL : MA3
MeCN < DMF < γ-BL : MA4

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 722-723

On Generalised Pair Potential-Binding Energy, Dissociation Energy and Electron Affinity of Alkali Halide Molecules

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Manuscript received 3 August 1979, revised 21 January 1980, accepted 31 March 1980

The generalised pair potential of Woodcock has been used to compare various properties of nineteen gaseous alkali halide molecules. These properties include binding energy, dissociation energy and electron affinity. The agreement between theoretical and experimental value is quite satisfactory showing the validity of the generalised pair potential.

THEORETICAL evaluation of molecular properties of alkali halide gaseous molecules using interaction potential has attracted the attention of a number of workers[1-14] during recent years. The aim of such calculation is to test the validity of the specific form of interaction potential by comparing the theoretically computed properties with experimental ones. Secondly the relative merits of the various empirical interionic potential functions can be assessed. In most cases two term potentials corresponding to a simple ionic model have been used. These two term potentials were found to be inadequate for experimental data on gaseous alkali halide ion pairs. In the year 1974, Woodcock[15] proposed a generalised three term potential and used this to compute various properties of gaseous alkali metal halides. Here in case of alkali halide molecules we have used the generalised pair potential of Woodcock which can be written as :

$$U_{(R)} = AR^{-m}\exp[-B(R^n-1)] - e^2R^{-1} \quad \dots (1)$$

where e is the electronic charge, R is the internuclear separation, A and B are the potential parameters and the values of m and n are different for different crystals In the present paper we have evaluated binding energy dissociation energy and electron affinity of alkali halide molecules using this generalised pair potential.

Theory :

Applying the familiar molecular stability and force constant condition[6,17]

$$\left.\begin{aligned} U'_{(R)} &= 0 \\ U''_{(R)} &= k_e \end{aligned}\right\} \text{ at } R = r_e \quad \dots (2)$$

to equation (1) one obtains

$$A = \frac{e^2}{r_e^{1-m}\exp[-B(r_e^n-1)]\,(m+n\,Br_e^n)} \quad \dots (3)$$

$$\text{and } B = [-x+(X^2-4YZ)^{\frac{1}{2}}]\,(2Y)^{-1} \quad \dots (4)$$

$$\text{where } x = r^n_e\left\{2\,mn-n^2-\frac{nr_e}{e^2}\,(k_e r_e^2+\frac{e^2}{r_e})\right\}$$

$$Y = n^2 r_e^{2n}$$

$$Z = m^2-\frac{mr_2}{e^2}\,k_e\,r_e^2+\frac{e^2}{r_e})$$

The binding energy D_i is given by

$$D_i = -U(r_e) \quad \dots (5)$$

$$\text{So that } D_i = \frac{e^2}{r_e}\,[1-\frac{1}{(m+nBr_e^n)}] \quad \dots (6)$$

The dissociation energy D_e, can be obtained from the equation

$$D_e = E - I + D_i \quad \dots (7)$$

Inserting the value of D_i from (6) one gets

$$D_e = E - I + \frac{e^2}{r_e}\,(1-\frac{1}{m+nBr_e^n}) \quad \dots (8)$$

where I is the ionisation potential of alkali atom, and E is the electron affinity of the halogen atom.

Results and Discussion

In order to calculate the various properties of alkali halide molecules the experimental values of r_e and k_e were taken from different sources[7,12,16,17]. The values of m and n are taken from the work of Woodcock. The calculated values of binding energy from equation (6) are listed in the second column of table. The experimental value of D_i are also given inthe third and fourth column for comparison. The agreement seems to be good considering the limitations in the theoretical approach and uncertainties involved in the experimental binding

TABLE 1—THEORETICAL AND EXPERIMENTAL VALUES OF BINDING ENERGY, DISSOCIATION ENERGY AND ELECTRON AFFINITY OF ALKALI HALIDE MOLECULES IN K. J./MOLE.

Mole-cules	D_i(Calc.)	D_i(exp) Ref(8)	D_i(obs) Ref(7)	D_e (calc)	D_e (exp)	E (cal)	E (mean)	E (exp)
LiF	727.1	745.8	770.3	534.1	574.1	367.0		
NaF	626.9	603.98	643.9	458.2	448.6	317.5		
KF	557.3	586.6	582.4	465.7	482.4	343.8	357.92	327*
RbF	536.6	548.99	558.98	460.8	516.2	382.5		324.4+
CsF	527.3	524.87	546.0	478.9	530.6	378.8		
LiCl	585.1	656.1	641.4	418 2	482.4	417.3		
NaCl	507.9	536.5	554.8	365.2	409.1	397.0		
KCl	456.7	480.5	493.7	391.1	424.4	386.4	396.66	353*
RbCl	442.7	466.98	474 5	392 9	434.2	394.4		348+
CsCl	431.1	445.8	469.9	408.7	443.8	388.2		
LiBr	545.9	619.4	618.4	321.1	419.7	393.8		
NaBr	481.1	515.2	534.3	280.5	366.6	381.3		
KBr	537.1	459.3	475.3	313.6	380.1	361.7	375.36	295.2*
RbBr	417.0	444.8	456.1	309.3	385.9	371.8		324.3+
CsBr	402.9	427.4	454.4	322.6	395.6	368.2		
LiI	499.3	580.8	580.3	289.0	337.7	358 4		
NaI	447.2	485.3	503 3	261.1	296.2	344.8		309.7*
RbI	388.7	414.9	426.3	295.5	323.2	337.4	342.2	295.4+
CsI	375.4	412.9	423.0	309.6	328.0	328.1		

Average % error -5.2%, -7.9%, -13.8%
*Schmidt Bocking & Bethge (1973)
+Berry & Reimen (1963)

energies. In the case of binding energy the mean percentage deviation between calculated and experimental values is not more than 7.9 percent. The calculated values of dissociation energy D_e according to Woodcock potential (1) using equation (8) are given in fifth column. The experimental values of dissociation energy are also listed in sixth column. The percentage deviation between theoretical and experimental values of dissociation energy is 13.8 percent. It is interesting to note that the calculated values of D_i and D_e are less than the observed values. The results of calculation can be improved if we consider the Van der Waals and dipole-quadrupole terms in the Woodcock potential. Such terms will give additional contribution to the interaction energy. The overall agreement is satisfactory. The electron affinity of halogen atoms were obtained from equation (8) and are recorded in the seventh column of the table. For the calculation of electron affinity, the experimental D_e values have been used. The average values of the electron affinity for halogens are compared with the experimental values of Schmidt-Bocking Bethge[21] and Berry-Reimann[22]. While calculating the values of D_i and D_e, the experimental values of E and I were taken respectively from the work of Bocking *et al*[21] and Massey[20]. The agreement between theoretical and experimental values of electron affinity is also satisfactory.

Acknowledgement

One of the authors (R.P.P.) is very grateful to U.G.C., New Delhi for providing the financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 724-727

Catalytic Studies on Nickel-Mordenite*

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Manuscript received 24 April 1978, revised 19 September 1978, accepted 30 October 1978

Molecular sieve zeolites are becoming increasingly important as catalysts for several major refining and petrochemical processes because of their structural features. These features are extensive interlattice pore volume, a pore size of molecular dimension, a large population of exchangeble cations within the interlattice pore volume. Mordenite zeolites are unique because of their two dimensional tubular structure, high stability and high selectivity for molecules of dimension 5.81 × 6.95 A.

Nickel-mordenite catalyst was prepared from sodium mordenite by ion exchange so as to get a good dispersion. Hydrogenation of benzene and dehydrogenation of cyclohexane were carried out on the reduced catalyst at different temperatures and hydrogen partial pressures. Turnover numbers and activation energies were calculated. The activities of nickel catalysts are compared. ESR studies were also made on mordenite catalysts.

MOLECULAR sieves are important as catalysts and as supports in petroleum and petrochemical industries due to their crystalline structure, definite pore size, large polar surface and remarkable thermal stability. Mordenite has a definite advantage over other zeolites because of its two dimensional pore structure and high silica-alumina ratio which is responsible for its thermal stability and sometimes higher catalytic activity. Particularly, the synthetic mordenites are free of stacking faults and are highly active for hydrocracking, hydroisomerization, alkylation, reforming and cracking-reactions which proceed through carbonium ion intermediates[1,2].

Catalytic sites are thought to be located at the cation sites or sites vacated by cations. Different cations can affect the catalytic properties of mordenite differently. In the present work a nickel-mordenite catalyst prepared from sodium mordenite by ion exchange which gives almost atomic dispersion of the metal, was used[3].

Hydrogenation of benzene and dehydrogenation of cyclohexane were selected as model reactions in characterizing the activity of nickel-mordenite catalyst because of the simplicity of reaction and the product formed could be easily analyzed and could directly be correlated with the activity of the catalyst.

ESR studies were also made on the mordenite catalyst to get an idea of the nature and the environment of the metal, atom in the catalyst.

Experimental

Sodium mordenite, Alite 150, 1.8 mm (lot 1695) extrudates supplied by L' Air Liquide, Paris was used. Fig. 1 gives the schematic diagram showing the formation of nickel-mordenite from sodium mordenite by ion exchange. Sodium mordenite was converted to its ammonium form by refluxing with aqueous ammonium nitrate at 90°. The ammonium mordenite thus formed is refluxed with nickel nitrate solution at 90°. The catalyst was washed well with water and dried at 110°. Nickel in the catalyst, estimated by atomic absorption spectroscopy, was found to be 0.5%. The sodium content was estimated by flame photometry (0.75%). The catalyst was reduced in flowing hydrogen (70 ml/min) at 400° for 6 hours.

A vertical tubular glass reactor was used. Reduced catalyst was crushed and only catalysts of mesh size 10-12 were used. Before each experiment the catalyst was reduced in flowing hydrogen at 400° for one hour. The products were analyzed by gas chromatography.

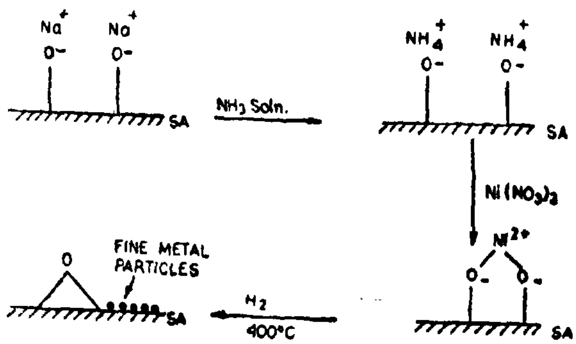


Fig. 1. Schematic diagram of cation exchange on mordenite.

*Presented at the Second National Symposium on Catalysis, I.I.T., Kharagpur, Dec. 1975.

Benzene hydrogenation was carried out in the temperature region 90-200° at LHSVs of 1.5 and 3.0 and at hydrogen/benzene mole ratios of 6.3 and 4.6 respectively. Turnover numbers were calculated for each experiment and the results are tabulated (Table 1). The dehydrogenation of cyclohexane was carried out in the temperature region 180-300° at LHSV 1.5, and at hydrogen/cyclohexane mole ratio of 7.6 (Table 2). Turnover number is defined as the number of cyclohexane molecules formed from benzene or the benzene molecules formed from cyclohexane per second per exposed atom of nickel.

A Varian E4 ESR spectrometer was used. The 'g' values were determined using DPPH as a calibrant (g=2.0036).

TABLE 1—HYDROGENATION OF BENZENE ON NICKEL-MORDENITE

Temp. °C	LHSV	Hydrogen/benzene mole ratio	Turnover Number $\times 10^{-6}$
90	3.0	4.6	8
110	3.0	4.6	11
130	3.0	4.6	14
160	1.5	6.3	24
200	1.5	6.3	30

TABLE 2—DEHYDROGENATION OF CYCLOHEXANE ON NICKEL-MORDENITE

Temp. °C	Turnover Number $\times 10^{-6}$
200	63.8
240	70.7
280	202.7

LHSV : 1.5
Hydrogen/cyclohexane mole ratio : 7.6

Results and Discussion

From Tables 1 and 2, one can see that the turnover number, which gives an idea of the specific catalytic activity, generally increases with temperature. However, there is a three fold increase in the turnover number for cyclohexane dehydrogenation at 280° compared to at 240°. This may be due to the availability of a larger metal surface for the reaction due to better activation at higher temperature in presence of atomic hydrogen produced during the dehydrogenation reaction itself.

The activation energies for benzene hydrogenation and cyclohexane dehydrogenation are 3.6 and 13.8 Kcals/mole respectively, in the temperature regions studied. The low activation energy for benzene hydrogenation suggests that the reaction is a diffusion controlled one. Since the feed rate is high (LHSV=3) and hydrogen/benzene mole ratio is also high (4.6), it may not be the bulk diffusion which is rate controlling. Either the intraparticle or the intrapore diffusion could be the rate determining step. Because the particle size is small enough it is likely that the intrapore diffusion is the rate controlling process.

In the metal loaded zeolite catalysts, by ion exchange, the metal is expected to be dispersed well inside the cavities[4]. For a given reaction to take place the sorbate molecule has to get into the pore so as to get in contact with the metal responsible for hydrogenation and dehydrogenation. Whether a sorbate molecule can enter a mordenite pore (5.81 × 6.95 A) depends on its critical dimension (smallest projected diameter). Benzene with a critical diameter of 6.8 A is just about the right size and can diffuse slowly into the mordenite cavity. The slow diffusion process may be the rate controlling step for benzene hydrogenation. Whereas, cyclohexane (critical diameter 6.1 A) which is smaller than benzene can enter the pores of mordenite easier than benzene, and the diffusion process may not be the rate controlling one. The reaction step could be the rate controlling one ; hence the higher activation energy.

In the Table 3 a nickel-silica-alumina catalyst[a] and the nickel-mordenite catalyst are compared for their catalytic activities. Nickel loading in silica-alumina catalyst was also done by ion exchange[5]. Eventhough, the nickel content in nickel-silica-alumina (2.2%) is higher than in nickel-mordenite (0.5%), there is a notable difference both in hydrogenation and dehydrogenation activities. May be, there are higher number of active sites present in nickel-mordenite than in the nickel-silica-alumina which is due to a better dispersion ability of mordenite compared to the amorphous silica-alumina. The absence of methyl cyclopentane as one of the products of catalytic reaction over nickel-mordenite is probably due to the presence of higher amount of sodium (0.75% by weight). Thus by varying the level of sodium content the selectivity of the nickel-mordenite catalyst for hydrogenation or dehydrogenation/isomerization can be controlled.

TABLE 3—COMPARISON OF THE ACTIVITIES OF NICKEL SILICA-ALUMINA AND NICKEL-MORDENITE

Catalyst	Temp. °C	Hydrogen/hydrocarbon mole ratio	Turnover Number $\times 10^{-6}$
Benzene hydrogenation			
NiSA	170	10	9.5*
NiSA	200	10	3.8*
NiM	160	6.3	24.0
NiM	200	6.3	30.0
Cyclohexane dehydrogenation			
NiSA	290	10	46.0*
NiM	280	7.6	202.0

(*) Calculated from Ref. (5)
Weight percentage of nickel in NiSA : 2.2
Weight percentage of nickel in NiM : 0.5

TABLE 4—SUMMARY OF ESR STUDIES ON MORDENITE CATALYSTS

Catalyst	g_1	g_2	Intensity Relative Ratio,	Intensity Relative Ratio,	Peak width (G) 1	Peak width (G) 2
1	-	2.38	-	3	-	1460
2	-	2.38	-	3	-	1400
3	2.19	-	9	-	410	-
4	2.28	2.48	42	27	680	1760
5	2.21	2.58	10	19	360	1200

Catalysts :

1. Fresh sodium mordenite powder, evacuated at 400° for 1 hour.
2. Unreduced nickel mordenite powder, evacuated at 400° for 1 hour.
3. Used nickel mordenite, regenerated in flowing oxygen at 400° for 2 hours and 500° for 2 hours : reduced in flowing hydrogen at 400° for 4 hours, evacuated at 400° for 1 hour.
4. Regeneration and reduction as for 3, passed 1% thiophene in cyclohexane at 280°, (4.5 ml/hr) for 1 hour, evacuated at 400° for 1 hour.
5. Used nickel mordenite, reduced in hydrogen (static) at 400° for 3 hours, evacuated at 400° for 1 hour.

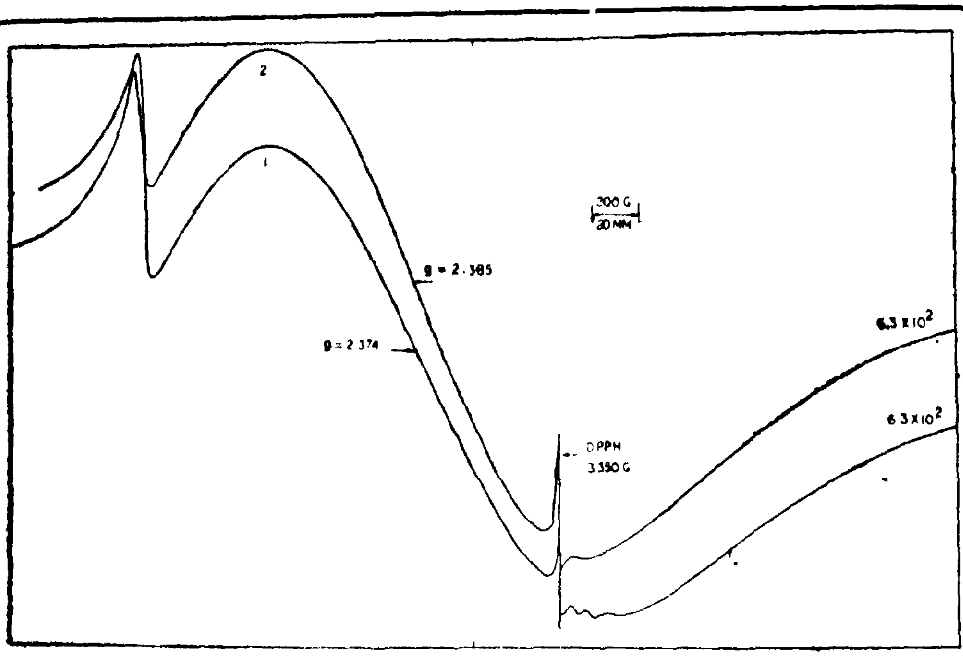


Fig. 2. ESR spectra of fresh sodium mordenite (1) and unreduced nickel mordenite (2)

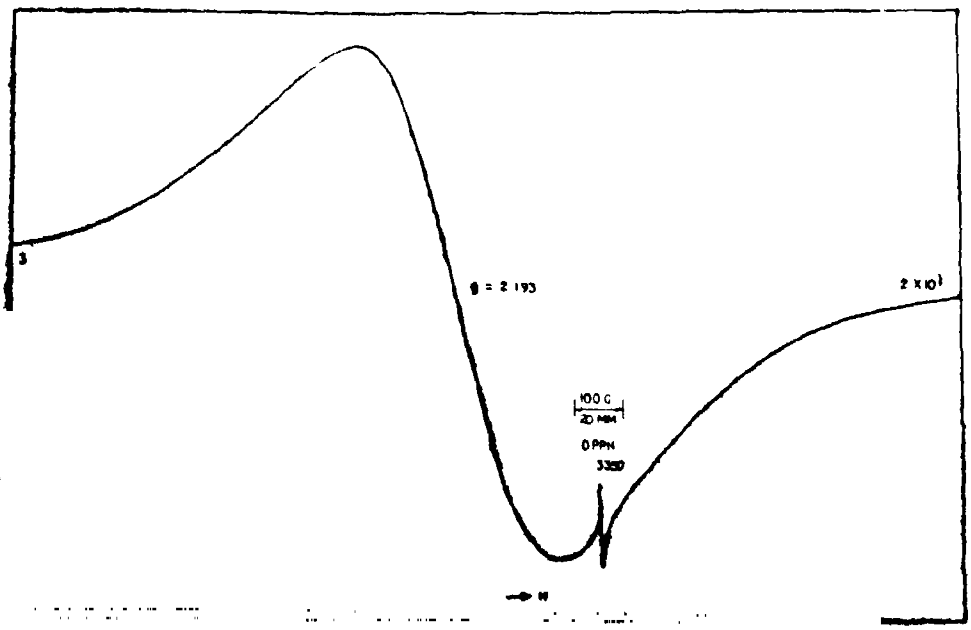


Fig. 3. ESR spectrum of reduced nickel mordenite (3)

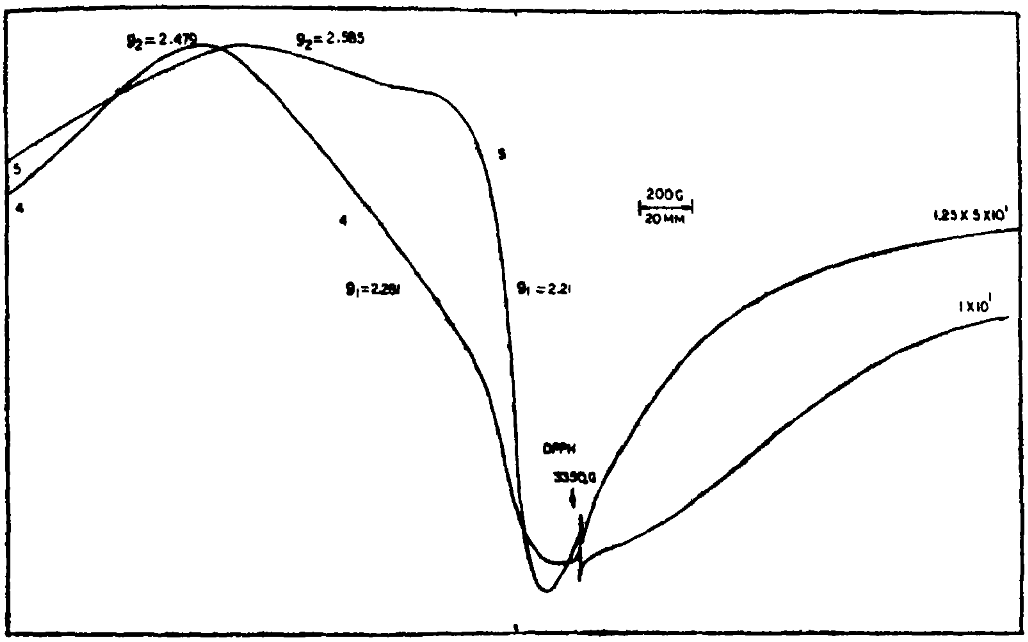


Fig. 4. ESR spectra of reduced nickel mordenite after 1% thiophene feed (4) and used nickel mordenite (5)

Table 4 gives the summary of ESR analysis. Fig. 2 shows the ESR spectrum of sodium mordenite (fresh) and unreduced nickel-mordenite. Both give signal, with 'g' value 2.38, which might be due to the presence of impurities such as Fe^{3+} and Mn^{2+} in mordenite itself[6,7] or due to some trapped electrons in the cavities. Reduced nickel-mordenite gives a sharp symmetric signal (Fig. 3) and the 'g' value of 2.19 corresponds to Ni^0 reported in the literature[8]. On the other hand the used catalyst (Fig. 4) gives two signals ('g_1'=2.21 and 'g_2'=2.59) with broadening of peak widths. Again, the thiophene treated catalyst (Fig. 4) gives two broad signals with 'g' values 2.28 and 2.48. Assigning the 'g' values of 2.21 and 2.28 in both the cases to Ni^0, the second broader signal may be due to partially oxidized impurities, or due to the trapped sulfur atoms, or due to the mordenite itself.

Acknowledgement

The author thanks Drs. I. B. Gulati and K. K. Bhattacharyya for encouragement and support.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 728-731

The Diffusion Control in Sol-Gel Transformation

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Manuscript received 8 January 1979, revised 12 October 1979, accepted 17 March 1980

Sodium alginate sol can be converted into ionotropic gel through the diffusion of a di- or trivalent metal ion. The kinetics of this process can be studied by two different methods. The first is the analytical method in which the decrease of the divalent metal ion concentration with time during the exchange process with sodium alginate sol is followed complexometrically. It is found that the rate of gel formation is greater at first during the primary gel membrane formation, and it depends on both the electrolyte and the sol concentration. The rate then decreases during the further gel growth and becomes constant whatever the concentration of the electrolyte is. This may be attributed to the diffusion control through the primary gel membrane.

The second method is the drop density method in which the rate of density variation of a sol drop during its contact with the electrolyte solution is taken as a measure of ionotropic gel growth. The drop density method is carried out at different temperatures, and the rate of growth is found to increase by raising temperature. The activation energy is calculated and found to have the values between (13-20 k.j./Mole).

SODIUM alginate is a poly-electrolyte, it consists of D-Mannuronic and L-guluronic acids[1].

Sodium alginate sol can be converted into ionotropic gel by the reaction with divalent or trivalent metal ions :

$$2\text{Na-alginate} + Cu(NO_3)_2 \rightleftharpoons Cu(\text{alginate})_2 + 2NO_3^- + 2Na^+$$

The sol-gel transformation is studied from the kinetic point of view. Ionotropic gels[2-7] can be formed by different methods depending on the way of diffusion of the electrolyte, either by ascending or descending technique which leads to the formation of gel disc, or by the radial diffusion of electrolyte which leads to the formation of a gel drop.

By using both techniques, the sol-gel transformation can be studied kinetically. The transformation of a sol drop to a gel has been studied by Awad *et al*[8].

In the present investigation, the kinetic studies are carried out by two different methods :

(a) *The drop density method* in which the variation of the sol drop density with time is taken as a measure of the rate of transformation. The gel formation is a partial discharge, and a partial dehydration process, which must lead to a change in density.

(b) *The analytical method* in which the concentration of the electrolyte used as a crosslinking material for the alginate molecule, changes with time. The decrease in the electrolyte concentration can be followed analytically.

Experimental

(a) *Materials* :

All materials used are of chemical grade. The water is double distilled. The temperature is controlled within 0.1° using an ultrathermostat.

(b) *Measurements and Calculations* :

Different sodium alginate sols are prepared by dissolving the proper amount in bidistilled water[9]. The water has to be stirred strongly, and then the solid alginate is added, otherwise, it gives a plumpy solution which swells with difficulty.

In the drop density method, a sol drop is allowed to fall from a small funnel. The sol drop floats on the electrolyte, as its density is smaller than that of the electrolyte containing the divalent cations. The drop floats till its density attains that of the electrolyte. At this time the drop starts to sink. The value of $\left(\frac{d\sigma_s}{dt}\right)$, the rate of the increase of the drop density is taken there as a function of the gel growth. Thus :

$$\frac{\sigma_e - \sigma_s}{\Delta t} = KV$$

where (σ_e) is the electrolyte density and

(σ_s) is the sol density.

For each sol and electrolyte concentration, the following precautions are taken into consideration to maintain the size of the sol drop constant as far as possible :

(1) The use of the same dropper.

(2) The height of the sol in the dropper as well as the distance from the dropper to the surface of the electrolyte is kept constant.

In the analytical method, a long wide tube of 1.5 cm radius is covered with a very thin layer of Na-alginate and then 2/3 of the tube is filled with the sol which is covered with $CuSO_4$ solution. As soon as copper sulphate solution comes in contact with the sol, a very thin gel membrane is promptly formed at the sol electrolyte interface which prevents their mixing. The change in the electrolyte concentration with time is followed by complexometric titration using titriplex[10]. Before each titration, air is bubbled in the electrolyte to ensure homogeneity of the electrolyte concentration above the sol to avoid the concentration gradient formed during the sol-gel transformation which takes place by the exchange process between sodium ions of the alginate sol and Cu^{2+} cations in the electrolyte. The value of $\left(\frac{-dC}{dt}\right)$ is thus the rate of the gel formation.

Results and Discussion

The density method results :

When a sol drop is allowed to fall into a divalent metal ion solution, a primary gel membrane which preserves the shape of the drop is formed. This drop remains at the electrolyte surface for a certain time through which the sol drop density grows up slowly to that of the electrolyte due to the Cu^{2+} ion diffusion into the sol drop through the primary membrane. The drop then begins to sink. The time consumed for the sol drop to start sinking down (t) is measured for different sol concentrations, and different electrolyte concentrations at different temperatures (30°, 40°, 50°, 60° and 70°).

The value $\frac{\sigma_e - \sigma_s}{\Delta t}$ is taken as function of the growth rate of the gel (rate of the sol-gel transformation).

Although the variation of the sol drop density (σ_s) with time is expected to be nonlinear during the formation of the primary gel membrane yet the value of $\frac{d\sigma_s}{dt}$ represents the velocity of this process.

So, the value of $\left(\frac{\quad}{dt}\right)$ can be practically considered as a function of the sol-gel transformation rate.

By varying the concentration of the electrolyte, the value of σ_e is controlled. The time (t) at which the drop starts to sink is plotted for the different electrolyte concentrations versus σ_e. The slope of the lines obtained is thus a function of the gel growth rate $\frac{d\sigma_s}{dt}$.

By repeating the experiment at higher temperatures 30°, 40°, 50°, 60° and 70°, it was found that the rate of the formation of the primary membrane as well as the further gel growth are enhanced very much. The slope obtained from growth plot $\left(\frac{d\sigma_s}{dt}\right)$ for sol 2% and $CuSO_4$ electrolyte (c.f. Figures 3, 4) was about 0.0028 at 30° and 0.01 at 70°.

The heterogeneous exchange reactions between Na^+ and Cu^{2+} ions (or any divalent cation), can thus be treated using the variation of density with time. The reaction, like many other heterogeneous reactions, was found to obey the power function.

$$V = K C^n \qquad \ldots \quad (1)$$

where (V) is the reaction velocity, (C) is the concentration of the varying reacting species, (K), and (n) are constants. As mentioned before $\left(\frac{\sigma_e - \sigma_s}{\Delta t}\right)$ can be considered as a function of V. So, by logarithming equation (1) we get.

$$\log V = K' + n \log C$$

or $\log\left(\frac{\sigma_e - \sigma_s}{\Delta t}\right) = K' + n \log C.$

Actually, by plotting $\log\left(\frac{\sigma_e - \sigma_s}{\Delta t}\right)$ versus log C, of the electrolyte, (as the varying species), straight lines were obtained with (n) value around (0.5). This value can be imagined physically as the order of the exchange reaction with respect to the divalent electrolyte (*Fig. 5*).

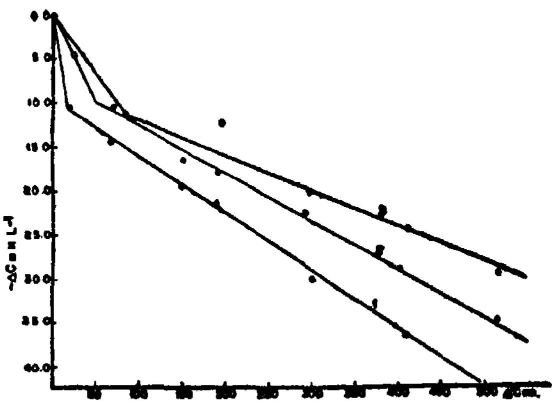


Fig. 1. The variation of Cu^{**} cation concentration with time during the exchange, with different sol concentrations t=25° 1-1.0%, 2-1.5% and 3-2.0%.

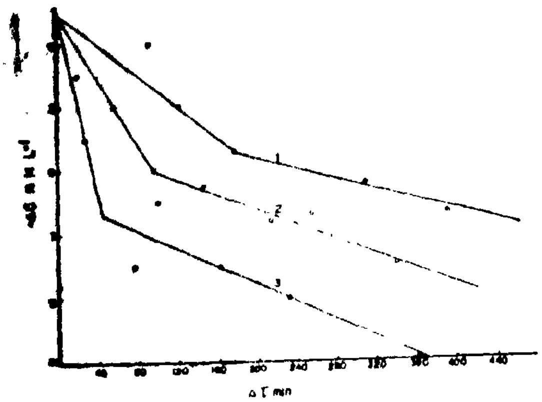


Fig. 2. The variation of Cu^{2+} concentration with time during the exchange with 2% sol. The initial concentration of Cu^{2+} are 1- 0.02*M*, 2- 0.06*M* and 3- 0.12*M*, t = 25°.

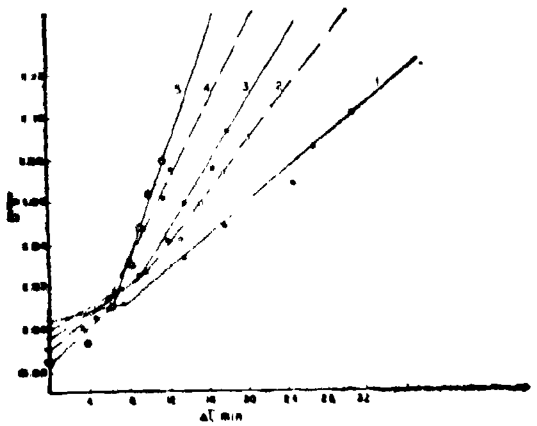


Fig. 3. The density of the sol drop (1%) with time in $CuSO_4$ solutions of different concentrations at temperatures 1-30°, 2-40°, 3-50°, 4-60° and 5-70°.

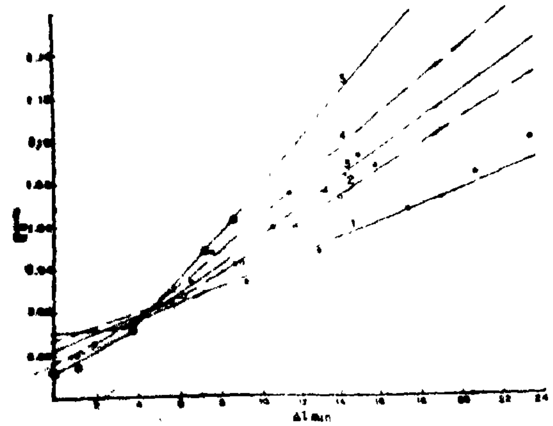


Fig. 4. The density growth of the sol drop 2% with time in $CuSO_4$ solutions of different concentrations at temperatures 1-30°, 2-40°, 3-50°, 4-60° and 5-70°.

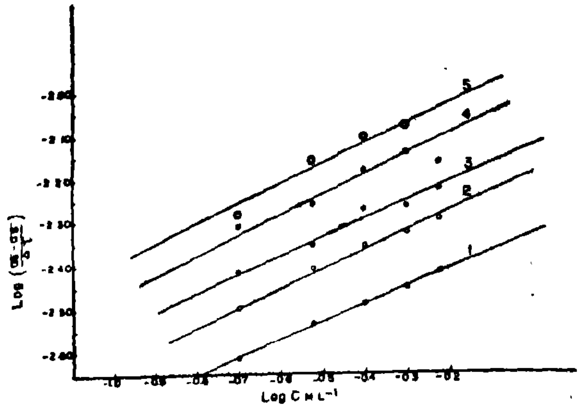


Fig. 5. The log $\frac{\sigma_c - \sigma_s}{\Delta t}$ gainst log C plots for 2% sol in $CuSO_4$ solutions, at temperatures, 1-30°, 2-40°, 3-50°, 4-60° and 5-70°.

By finding out different values of $\left(\frac{d\sigma}{dt}\right)$ for a definite sol and electrolyte concentration at different temperatures, the activation energy of the process (E) can be calculated (Table 1). From this table, it is clear that the value of the activation energy, lying in the range (13—20 K.J./Mole), indicates that the process is a diffusionally-controlled one.

TABLE 1—ACTIVATION ENERGIES FOR Cu^{2+} IN K.J./MOLE

C_{sol}	C (electrolyte)				
	0.2*M*	0.3*M*	0.4*M*	0.5*M*	0.6*M*
1%	14.446	17.25	20.013	19.324	19.69
1.5%	13.359	17.15	16.247	15.66	16.67
2%	16.189	17.309	18.078	17.58	15.93

The analytical method results :

The decrease in the concentration of (Cu^{2+}) ions with time, for the different concentrations of sol and electrolyte is shown in Figures (1, 2). From these figures, it is quite evident that the rate of gel formation (the exchange process between Na^+ ions in the sol and Cu^{2+} ions in the electrolyte) is greater at first and then it decreases. Two definite slopes of the linear relation (-dC/dt) are recognized on these curves. The first slope is much greater than the second one. This means that the rate of gel growth i.e., the rate of ion exchange, or, the rate of the formation of the primary gel membrane (the most outer membrane which will be formed promptly at the moment of contact between the sol and electrolyte) is much higher at first, and then it decreases and that decrease becomes almost constant. At the

early stages of gel formation the rate was found to depend on both Cu^{2+} ion and sol concentrations. The second slope was found to depend only on the sol concentration. This fact can be explained on the basis of the diffusion control of the exchange process.

The formation of the primary gel membrane does not need considerable diffusion of the cations (Cu^{2+}) inside the sol, thus this process depends on both electrolyte and sol concentrations. It is faster in the higher electrolyte, and lower sol concentrations. Further growth of the gel takes place by the diffusion of the Cu^{2+} cations, through this primary membrane The last process is greatly hindered by the viscosity of the sol, and the compactness of the already formed gel membrane. That is why, the rate of gel formation (second rate), is almost independent of the electrolyte concentration, and oppositely proportional to the sol concentration, due to the marked dependence of the viscosity on the sol concentration.

By plotting log $\frac{\sigma - \sigma}{\Delta t}$ versus $\frac{1}{T}$, straight lines were obtained indicating the validity of our suggestion that the change of density with time can be considered as a measure of the gel growth rate.

Thus, the suggested technique and calculations may be of significant value in the kinetic studies of sol-gel transformation processes.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 732-735

Polarographic Studies on the Influence of Aqueous Mixtures of Some Organic Solvents on the Kinetics of Irreversible Electrode Reaction of Nitrobenzene

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Manuscript received 20 October 1978, revised 21 August 1979, accepted 9 February 1980

The polarographic behaviour of nitrobenzene in McIlvaine (McI) buffer of pH values 3.2 and 8 has been studied in the presence of aqueous mixtures of methanol, ethanol, dimethylformamide and acetonitrile. The reduction of nitrobenzene has been found to be diffusion-controlled and irreversible at different percentages of organic solvents. The kinetic parameters (αn_a and $k^o_{f,h}$) of irreversible electrode reaction of nitrobenzene have been calculated by Koutecky's method at different percentages of these organic solvents A decrease in the value of kinetic parameters with increasing amounts of organic solvents indicates that the irreversible electrode reaction of nitrobenzene is rendered increasingly more irreversible. A negative shift in $E_{1/2}$ values and an increase in the value of $\Delta G^{\neq}$, the free energy of activation, support this conclusion.

VIJAYALAKSHAMMA and Subrahmanya[1-3] have studied the polarographic behaviour of nitrobenzene in aqueous mixtures of ethanol, acetonitrile, acetone and dioxane with a view to determining the polarographic characteristics viz., $E_{1/2}$, i_d and D, as a function of the percentage of organic solvent. They have also calculated kinetic parameters for the irreversible electrode reaction of nitrobenzene at different percentages of these solvents. However, these studies are still incomprehensive in as much as that the influence of the organic content of the aqueous mixture on the kinetics of the electrode reaction has not been explained explicitly. With this aim in view a polarographic study of the electrode reaction of nitrobenzene in the presence of aqueous mixtures of methanol, ethanol, dimethylformamide and acetonitrile has been undertaken.

Materials and Methods :

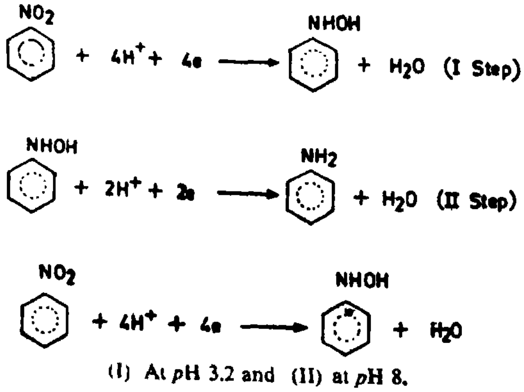
All the chemicals used were either of A. R., B.D.H., or E. Merck, G. R. grade. The concentration of nitrobenzene was maintained at $1.0 \times 10^{-3} M$. Triton X-100 (1.6×10^{-3}%) was used as a maximum suppressor. A manual polarograph (Toshniwal, CL02) in conjunction with a polyflex galvanometer (Toshniwal, PL50) was used. All the measurements were made at $25 \pm 0.1°$. Purified nitrogen was used for removing the dissolved oxygen. The potentials were measured against a saturated calomel electrode (S.C.E.). The d.m.e. had the following characteristics (in 0.1 M KCl, open circuit at 25°). h_{corr} = 73.12 cms, t = 3.60 sec, $m^{2/3} t^{1/6}$ = 2.672 $mg^{2/3} sec^{-1/2}$.

The number of electrons (n) involved in the reduction process was determined by millicoulometric method of DeVries and Kroon[4] using a mercury pool cathode. This gave the value of n equal to 4 for the first step reduction and 2 for the second step. Having known the value of n, Ilkovic equation was used to calculate the value of D, the diffusion coefficient of nitrobenzene at different percentages of the organic solvents.

The potential dependent rate constant $k_{f,h}$ was calculated by Koutecky method[5,6]. Having calculated $k_{f,h}$ at various stages of the wave, the parameters αn_a and $k^o_{f,h}$ were calculated from log $k_{f,h}$ vs $E_{d.e.}$ plots[7].

Results and Discussion

At pH 3.2 nitrobenzene in aqueous mixtures of ethanol (10%–50%) gives well defined 2—step reduction waves while at pH 8 only one step appears. The reduction mechanism at these pH values is as follows :



(I) At pH 3.2 and (II) at pH 8.

However, in the case of aqueous mixtures of methanol and dimethylformamide at *p*H 3.2 the second step does not appear at percentages≥50 (Fig. 1) while in acetonitrile the second step does not appear at percentages≥25. At *p*H 8 one step reduction wave of nitrobenzene does not show any deformation as the percentage of the organic solvent is increased (Fig. 2).

The wave-heights are diffusion-conrtolled at all percentages of organic solvents as evidenced by the linearity of i_d vs $h^{1/2}_{corr}$ plots.

On applying various criteria of irreversibility[8-10] it has been ascertained that the reduction of nitrobenzene is totally irreversible at different percentages of organic solvents.

Table 1 includes the polarographic characteristics of nitrobenzene in the presence of increasing percentages of organic solvents. A perusal of this table reveals that a significant negative shift in $E_{1/2}$ values occurs as the percentage of organic solvents is increased.

TABLE 1—POLAROGRAPHIC CHARACTERISTICS OF NITROBENZENE IN AQUEOUS MIXTURES OF ORGANIC SOLVENTS IN MCI BUFFER OF DIFFERENT *p*H VALUES

[Solvent] % (v/v)		I step i_d μA	I step $-E_{1/2}$ V (S.C.E.)	Slope mV	II step i_d μA	II step $-E_{1/2}$ V (S.C.E.)	Slope mV	D × 10⁶ cm²/sec.
				*p*H 3.2				
Dimethyl-formamide	10	17.56	0.33	82.14	4.08	0.88	200.00	3.89
	25	15.25	0.42	80.76	2.13	0.98	188.23	2.76
	50	14.55	0.58	118.18	-	-	-	1.65
				*p*H 8				
Dimethyl-formamide	10	15.61	0.69	76.47	-	-	-	4.27
	25	15.25	0.80	90.00	-	-	-	4.08
	50	10.46	0.94	90.00	-	-	-	1.92
				*p*H 3.2				
Ethanol	10	15.68	0.30	57.14	6.58	0.84	140.00	3.92
	25	14.97	0.35	70.00	6.10	0.91	96.29	3.50
	50	16.74	0.56	155.17	5.65	1.07	83.80	3.76
				*p*H 8				
Ethanol	10	15.26	0.64	81.81	-	-	-	4.08
	25	13.13	0.70	77.77	-	-	-	3.02
	50	13.13	0.84	110.00	-	-	-	3.02
				*p*H 3.2				
Acetonitrile	10	17.03	0.31	69.23	4.43	0.86	146.66	3.60
	25	20.58	0.39	90.90	-	-	-	3.30
	50	24.12	0.55	105.26	-	-	-	4.54
				*p*H 8				
Acetonitrile	10	17.38	0.65	68.42	-	-	-	5.30
	25	17.74	0.74	75.00	-	-	-	5.52
	50	25.19	0.88	125.00	-	-	-	11.14
				*p*H 3.2				
Methanol	10	18.08	0.29	70.58	6.16	0.78	177.77	4.70
	25	15.21	0.31	62.50	5.75	0.86	233.33	3.61
	50	20.55	0.43	109.90	-	-	-	7.40
				*p*H 8				
Methanol	10	13.15	0.58	70.58	-	-	-	3.02
	25	12.74	0.64	70.00	-	-	-	2.82
	50	15.62	0.75	100.00	-	-	-	4.28

TABLE 2—VALUES OF KINETIC PARAMETERS (α, αn_a AND $k^0_{f,h}$) AND OF $\Delta G^{\ddagger}$ IN AQUEOUS MIXTURES OF ORGANIC SOLVENTS IN McI BUFFER OF DIFFERENT pH VALUES

[Solvent] % (v/v)		αn_a	α	I step $k^0_{f,h}$ cm/sec	$\Delta G^{\ddagger}$ k cal mole^{-1}	αn_a	α	II step $k^0_{f,h}$ cm/sec	$\Delta G^{\ddagger}$ k. cal. mole^{-1}
					pH 3.2				
Dimethyl-formamide	10	0.68	0.38	7.60×10^{-6}	12.22	0.40	0.20	8.05×10^{-7}	13.49
	25	0.59	0.29	6.29×10^{-6}	12.56	0.38	0.19	2.80×10^{-7}	14.93
	50	0.35	0.27	7.26×10^{-7}	14.44	-	-	-	-
					pH 8				
Dimethyl-formamide	10	0.76	0.38	9.12×10^{-9}	16.00	-	-	-	-
	25	0.60	0.30	1.92×10^{-9}	17.33	-	-	-	-
	50	0.57	0.28	6.48×10^{-11}	19.42	-	-	-	-
					pH 3.2				
Ethanol	10	0.96	0.48	$2.07 \times 10^{-}$	10.93	0.59	0.29	1.90×10^{-8}	16.00
	25	0.77	0.38	1.00×10^{-5}	11.84	0.52	0.26	6.60×10^{-9}	16.80
	50	0.68	0.34	2.56×10^{-6}	12.87	0.48	0.24	6.84×10^{-11}	19.61
					pH 8				
Ethanol	10	0.73	0.36	1.03×10^{-8}	16.01	-	-	-	-
	25	0.64	0.32	6.05×10^{-9}	16.55	-	-	-	-
	50	0.53	0.26	3.04×10^{-9}	17.23	-	-	-	-
					pH 3.2				
Acetonitrile	10	0.73	0.36	1.16×10^{-4}	8.94	0.35	0.17	2.22×10^{-7}	15.14
	25	0.59	0.29	1.62×10^{-5}	10.64	-	-	-	-
	50	0.56	0.28	3.26×10^{-7}	14.39	-	-	-	-
					pH 8				
Acetonitrile	10	0.78	0.39	3.82×10^{-9}	16.47	-	-	-	-
	25	0.70	0.35	1.25×10^{-10}	18.70	-	-	-	-
	50	0.51	0.25	1.00×10^{-10}	19.31	-	-	-	-
					pH 3.2				
Methanol	10	0.78	0.39	3.88×10^{-5}	11.00	0.33	0.16	4.84×10^{-7}	14.74
	25	0.72	0.36	2.34×10^{-5}	11.46	0.30	0.15	1.65×10^{-7}	15.45
	50	0.51	0.25	8.63×10^{-6}	12.58	-	-	-	-
					pH 8				
Methanol	10	0.80	0.40	4.78×10^{-9}	16.29	-	-	-	-
	25	0.74	0.37	9.42×10^{-10}	17.40	-	-	-	-
	50	0.66	0.33	8.69×10^{-10}	17.65	-	-	-	-

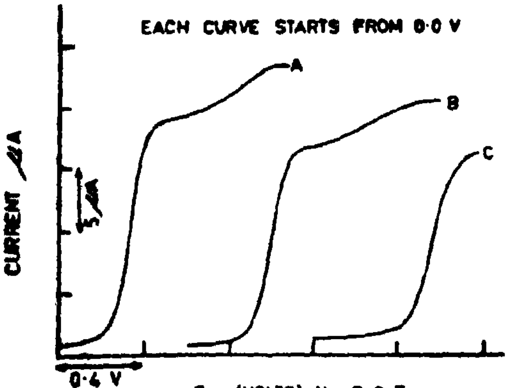


Fig. 1. Polarograms of nitrobenzene in different percentages of dimethylformamide at pH 3.2. (A) 10% (B) 25% (C) 50%

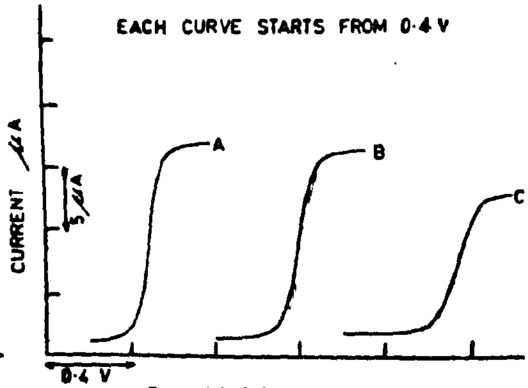


Fig. 2. Polarograms of nitrobenzene in different percentages of dimethylformamide at pH 8. (A) 10% (B) 25% (C) 50%

In Table 2 the values of kinetic parameters (αn_a and $k^o_{f,h}$) and also of $\Delta G^{\ddagger}$ have been listed. According to Vijayalakshamma and Subrahmanya[1], since n_a, the number of electrons involved inthe rate determining step for nitrobenzene is 2, the value of α can be obtained from the corresponding values of αn_a at different percentages of organic solvents and these have been also included in Table 2. A perusal of this table shows that both α and $k^o_{f,h}$ record a decrease with increasing percentage of organic solvents thereby suggesting[11-14] that the electrode reaction of nitrobenzene is rendered increasingly more irreversible. A negative shift in $E_{1/2}$ and an increase in the value of $\Delta G^{\ddagger}$, with increasing percentages of organic solvents lend support to this conclusion.

Acknowledgement

Thanks are due to the Principal, Agra College, Agra for providing necessary facilities.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp.736-739

Influence of Pesticides on the Trace Element Status of Soils (BHC on Manganese and Iron)

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Manuscript received 21 September 1978, revised 24 January 1980, accepted 9 April 1980

The effects of different doses of hexachlorocyclohexane (BHC), a well known insecticide, on the Mn and Fe status of a saline sodic soil were examined. The results revealed that 0.25 g of BHC per kg of soil after an interval of 30 days produced optimum effect on trace element status. At this dose and time interval water soluble Mn, exchangeable Mn, active Mn, exchangeable and available Fe significantly increased while reducible Mn decreased. The effect of the chemical started declining after a period of 4 weeks of application. The responses have been explained on the basis of chemical and microbial activity in soil.

PESTICIDES are widely used in agricultural production. They are used as insecticides, herbicides, fungicides and nematocides. The importance of pesticides in crop production is due to their accumulation in soils and their effect on soil properties. Several workers[1-6] have studied this subject in considerable detail, but information on the influence of pesticides on the trace element status is lacking.

Mn^{2+} exists in soil as a water soluble and as exchangeable ion and hence in this state is available to plants. Mn^{4+} exists as unavailable form but is reducible to available form. Manganese along with iron assists in formation of chlorophyll and control many complicated systems of oxidation-reduction in plants and soils. Iron exists as Fe^{2+} and Fe^{3+} and its availability is governed by oxidation-reduction potential of the soil. Micro-organisms are mainly responsible for iron transformation.

Hexachlorocyclohexane (BHC) is widely used as an insecticide to control insect pests. In view of the great importance of the trace elements in plants metabolism and the increasing use of pesticides for high crop yields, it was considered that an examination of the effects of BHC on manganese and iron transformation in a saline sodic soil would be useful.

Experimental

The soil used in the study (depth 0-30 cm) was collected from a representative area of Aligarh district. It was dried, crushed and seived. The general physicochemical characteristics of the soil were determined and yielded the following data : $pH = 8.80$, electrical conductivity $= 4.5 \times 10^{-4}$ mhos cm^{-1}, organic matter = 0.41%, water soluble Mn = 3.2 ppm, exchangeable Mn = 8.8 ppm, reducible Mn = 61.4 ppm, exchangeable Fe = 11.9 ppm and available Fe = 38.5 ppm.

The experiments on the influence of pesticide on the trace elements were done in earthenware pots of 20×20 cm size. They were cleaned and fitted with polythene sheets on the wall of pots towards the inner side to prevent absorption of water. One kg of the soil was then placed in each of the twenty one pots. Seven doses of BHC (0.0, 0.1, 0.2, 0.25, 0.3, 0.4, 0.5 g) were then added and mixed with 1 kg of soil in three replications without growing any crop. All the samples were then watered upto the water holding capacity with distilled water every week throughout the period of experiment. The treated samples were sampled at intervals of fifteen days and were analysed for exchangeable, water, soluble and reducible Mn and for exchangeable and available Fe.

The *p*H and electrical conductivity were measured in 1 : 5 soil water suspension at $25 \pm 1°$. Organic matter was estimated as per Walkley and Black's[7] method.

Water soluble, exchangeable and reducible Mn were estimated colorimetrically according to Jackson[8] using Leeper's method as modified by Sherman and Harmer[9] with normal ammonium acetate (*p*H-7) as extractant and 85% orthophosphoric acid and potassium periodate as colour reagents. A 2% hydroquinone solution of normal ammonium acetate was used as extractant for reducible manganese. The absorbance was recorded using a Bausch and Lomb spectronic '20' reading at 525 nm. Exchangeable and available iron were determined spectrophotometrically by Saywell's[10] method using normal ammonium acetate (*p*H-7) and ammonium acetate (*p*H-4.8) as extractant respectively ; and hydroxylamine hydrochloride and orthophenanthroline as colour reagents. Absorbance was recorded at 490 nm. Blanks were used in all the cases.

The data were subjected to statistical analysis of variance according to the two way classification with one observation per cell, the null hypothesis being the equality of the effects of different doses and different time intervals. Correlation coefficients were also calculated.

Results and Discussion

The data on the water soluble, exchangeable, reducible and active Mn in presence of BHC with different doses at various time intervals ot time are represented in Tables 1 to 4. Results for exchangeable and available Fe are recorded in Tables 5 and 6. Each datum in the table is a mean of triplicate values.

The results show that with the application of BHC there was no significant change in *p*H and electrical conductivity of the soil.

TABLE 1—EFFECT OF BHC ON WATER SOLUBLE MANGANESE OF SOIL WITH VARIATION IN CONCENTRATION AND TIME

Doses in g per kg of soil	Water soluble manganese in ppm at various days: 1	15	30	45	60	75	90	Average
0.00	3.26	4.43	5.68	5.00	4.54	3.95	3.35	4.32
0.10	3.23	5.69	7.50	6 82	6.25	5.56	5.00	5.72
0.20	3.22	6.87	8.75	7.89	7.14	6.58	6.00	6.64
0.25	3.26	8.06	10.71	10.00	9.09	7.89	7.30	8.05
0.30	3.20	6.82	8.33	7.50	6.97	6.25	5.70	6.39
0.40	3.23	5.98	7.50	6.67	6.10	5.71	5.10	5.75
0.50	3.22	5.00	6.58	5.98	5.55	4.76	4.20	5.04
Average	3.23	6.12	7.86	7.12	6.52	5.81	5.26	

Variance ratio and L.S.D. for days = 61.84, 0.292.
Variance ratio and L.S.D. for dosage = 41.46, 0.292.

TABLE 2—EFFECT OF BHC ON EXCHANGEABLE MANGANESE OF SOIL WITH VARIATION IN CONCENTRATION AND TIME

Doses in g per kg of soil	Exchangeable manganese in ppm at various days: 1	15	30	45	60	75	90	Average
0.00	8.90	13.75	16.00	14.38	13.75	13.00	12.50	13.18
0.10	8.85	15.00	19.38	16.50	15.79	15.00	14.00	14.93
0.20	8.94	19.38	21.25	20.00	19.23	18.46	16.70	17.71
0.25	8.90	22.50	25.00	22.00	21.25	20.64	19.80	20.01
0.30	8.96	20.00	22.00	19.38	18.44	17.84	17.00	17.66
0.40	8.98	18.75	20.00	18.00	17.07	16.32	15.60	16.39
0.50	8.92	14.32	17.50	15.00	14.26	13.52	12.90	13.76
Average	8.92	17.68	20.16	17.89	17.11	16.39	15.50	

Variance ratio and L.S.D. for days = 54.75, 0.721.
Variance ratio and L.S D. for dosage = 25.90, 0.721.

TABLE 3—EFFECT OF BHC ON REDUCIBLE MANGANESE OF SOIL WITH VARIATION IN CONCENTRATION AND TIME

Doses in g per kg of soil	Reducible manganese in ppm at various days: 1	15	30	45	60	75	90	Average
0 00	61.74	56.82	55.52	57.26	57.91	58.05	58.15	57.92
0.10	61.94	56.19	54.37	57.20	57.40	57.82	58.80	57.69
0.20	61.53	53.68	52.33	53.67	54.59	54 87	56.30	55.28
0 25	61.90	51.08	48.83	50.89	51.69	52.00	52.40	52.68
0.30	61.71	52.42	51.70	53.37	53.82	54.15	54.30	54.50
0.40	61.85	53.21	53.38	55.26	55.87	56.09	56.80	56.07
0.50	61.89	56.91	54.16	56.70	57.27	58.22	58.40	57.65
Average	61.79	54.33	52.90	54.91	55.52	55.89	56.45	

Variance ratio and L.S.D. for days = 25.21, 0.836.
Variance ratio and L.S.D. for dosage = 10.50, 0.836.

TABLE 4—EFFECT OF BHC ON ACTIVE MANGANESE OF SOIL WITH VARIATION IN CONCENTRATION AND TIME

Doses in g per kg of soil	Active manganese in ppm at various days: 1	15	30	45	60	75	90	Average
0.00	73.90	75.00	77.20	76.64	76.20	75.00	74.00	75.42
0.10	74.02	76.88	81.25	80.52	79.53	79.38	77.80	78.48
0.20	73.69	79.93	82.33	81.56	80.96	79.93	79.00	79.63
0.25	74.06	81.64	84.54	82.89	82.03	80.52	79.50	80.74
0.30	73.87	79.24	82.03	80.25	79.23	78.24	77.00	78.55
0.40	74.06	77.94	80.88	79.93	79.04	78.12	76.50	78.07
0.50	74.03	76.29	78.24	77.68	77.08	76.50	75.50	76.45
Average	73.95	78.13	80.92	79.92	79.16	78.24	77.04	

Variance ratio and L.S.D. for days = 22.24, 0.744.
Variance ratio and L.S.D. for dosage = 10.80, 0.744.

An examination of Table 1 showed that compared to control, water soluble Mn increased significantly. Maximum value reached with 0.25 g of BHC at 30 days and then declined. The increase in water soluble Mn was 10.7 ppm from 3.2 ppm. The influence of the doses was in the order 0.25>0.2>0.3>0.4>0.1>0.5>0.0 g of BHC per kg of soil. Similar results with variable intensity were observed in exchangeable and active Mn (Tables 2 and 4). With the 0.25 g dose of BHC the increase in exchangeable Mn was 25.0 from 8.9 ppm and in active Mn from 74.0 to 84.5 ppm at an interval of 30 days. The influence of the doses for exchangeable Mn was in the order 0.25>0.3>0.2>0.4>0.1>0.5>0.0 g of BHC per kg of soil and 0.25>0.2>0.3>0.1>0.4>0.5>0.0 g for active Mn.

Various workers[11] have reported the mechanisms by which an increase in availability of water soluble, available and active Mn occurred in fumigated and unamended soil. The fact that all the three forms of Mn simultaneously increased and then declined showed an effect of both biological and chemical factors on the Mn status of the soil under study. Aligarh soils have been found to contain hard nodular concretions of manganiferous deposits[12].

The increase in water soluble, available and active Mn occurred, may be due to the solubilising effects caused by soil fungi *Aspergillus niger*[13] and/or bacteria *Thiobacillus*; the liberation of Mn from organic matter by the stimulated activity of fumigant resistant bacteria which led to decomposition of organic matter as the soil was wetted with water. These results found support, with the work of Wensley[14] and Martin *et al.*[15], who reported an enhanced microbial activity in soils as a result of fumigation; with the work of Klemmer[16] who noticed that lower doses of certain eradicant type chemicals produced greater, reinvasion potentials in soils; and with the results of Smith[11] who found an increase in water soluble and available Mn^{2+} on fumigation. With the toxic effect of higher doses of the chemical on the soil micro-organisms, the stimulated effect declined after a certain period, and the equilibrium shifted towards Mn^{4+} resulting in a decrease of Mn^{2+} form (Table 3). The decline in water soluble and exchangeable Mn with passage of time appeared, may be due to the dissipation of the organic chemical with re-establishment of pesticide sensitive Mn oxidising bacteria such as *Bacillus, Actinomycetes, Aerobactor* etc. The results were in agreement with the findings of Charles and Paul[17].

Correlation coefficient data also supports the above conclusions. Thus while exchangeable Mn was positively correlated to water soluble form ($r^2=0.973$), there was a negative correlation between exchangeable and reducible Mn ($r^2 = -0.971$).

An examination of Tables 5 and 6 showed that exchangeable and available Fe significantly increased, reached a maximum value with 0.25 g dose of BHC at 30 days of its application and then decreased significantly. The effect of the doses on the increase of exchangeable Fe was 0.25>0.2>0.3>0.4>0.1>0.5>0.0 g BHC per kg soil and 0.25>0.3>0.2>0.1>0.4>0.5>0.0 g for available Fe. The maximum increase for exchangeable Fe was 25.0 ppm from 12.2 ppm (Table 5) and 58.9 ppm from 39.4 ppm for available Fe (Table 6).

TABLE 5—EFFECT OF BHC ON EXCHANGEABLE IRON OF SOIL WITH VARIATION IN CONCENTRATION AND TIME

Doses in g per kg of soil	Exchangeable iron in ppm at various days 1	15	30	45	60	75	90	Average
0.00	12.14	14.29	16.42	15.22	14.65	13.57	12.90	14.17
0.10	12.22	17.14	19.28	18.02	17.49	16.37	15.70	16.60
0.20	12.35	19.99	22.50	21.42	20.71	19.29	18.50	19.25
0.25	12.24	21.89	25.00	23.57	22.14	20.72	20.00	20.79
0.30	12.14	19.46	22.14	21.04	19.19	18.92	18.10	18.83
0.40	12.55	18.03	20.71	19.73	18.75	17.35	16.50	17.66
0.50	12.34	16.60	19.11	18.03	17.14	15.73	15.00	16.28
Average	12.28	18.20	20.74	19.58	18.90	17.42	16.57	

Variance ratio and L.S.D. for days—42.50, 0.640.
Variance ratio and L.S.D. for dosage—26.37, 0,640.

TABLE 6—EFFECT OF BHC ON AVAILABLE IRON OF SOIL WITH VARIATION IN CONCENTRATION AND TIME

Doses in g per kg of soil	Available iron in ppm at various days 1	15	30	45	60	75	90	Average
0.00	39.40	47.14	50.00	48.58	47.17	46.34	45.50	46.30
0.10	39.34	49.27	52.13	50.00	48.58	47.62	47.80	47.82
0.20	39.78	51.40	54.97	52.84	50.71	49.96	49.00	49.81
0.25	39.42	54.95	58.92	54.66	53.53	53.44	51.60	52.22
0.30	39.57	52.09	55.37	52.23	50.81	49.88	49.00	49.85
0.40	39.34	49.96	52.09	50.67	48.54	47.62	46.80	47.86
0.50	39.42	42.73	49.96	48.54	46.31	45.60	44.80	46.05
Average	39.47	50.36	53.35	51.07	49.38	48.49	47.78	

Variance ratio and L.S.D. for days—501.25, 0.300.
Variance ratio and L.S.D. for dosage—124.94, 0.300.

TABLE 7—CORRELATION COEFFICIENTS BETWEEN DIFFERENT FORMS OF MANGANESE AND IRON

Sl. No.	Form	Water soluble Mn	Reducible Mn	Exchangeable Fe	Available Fe
1.	Exchangeable Mn	0.973	-0.971	0.976	0.978
2.	Water soluble Mn	-	-0.930	-0.973	-0.971
3.	Reducible Mn	-	-	-0.932	-0.956
4.	Exchangeable Fe	-	-	-	0.936

An examination of Table 7 showed that there existed significant positive correlation between exchangeable Mn and exchangeable and available Fe ($r^2=0.976$ and 0.978 respectively) as well as between water soluble Mn and exchangeable and available Fe ($r^2 = 0.973$ and 0.971 respectively). There was also a positive correlation between exchangeable and available Fe ($r^2 = 0.936$). The exchangeable and available Fe, however, were negatively and significantly correlated to reducible Mn ($r^2 = -0.932$ and -0.956 respectively).

The above results pointed to the fact that conditions affecting Fe and Mn availability in soils were of similar type, a view in accordance with results of Smith[11]. It appeared that, reducible character of organic matter in soil and its microbial decomposition with liberation of acids, the drop in oxidation-reduction potential in moist conditions of the soil, stimulation in the activity of micro-organism by pesticides extending upto a period of about 30 days and favourable *p*H[19] all contributed towards an increase in exchangeable and available Fe. The decline in available and exchangeable Fe with passage of time appeared, may be due to the fact that with dissipation of the organic chemical, the stimulatory effects decline ; and Fe bacteria take over both the forms. Same results were also observed by Pringsheim[19,20] and Alexander[3].

Acknowledgement

Authors are thankful to Dr. S. S. Gupta, Principal and Dr. H. Singh, Dept. of Chemistry, for encouragement, cooperation and helpful suggestions.

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J. Indian Chem. Soc.,
Vol. LVII, July, 1980 pp. 740-741

Synthesis of Coumaron/Coumarinyloxyacetyl Ureas

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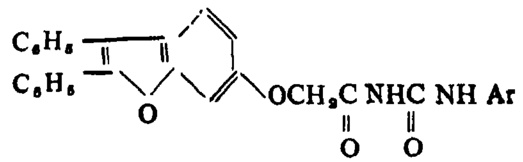
Manuscript received 21 August 1979, revised 29 January 1980, accepted 9 April 1980

Some new N[1]-(2,3-diphenyl coumaron-6-yloxyacetyl)-N[3]-arylureas and N[1]-(4-methyl coumarin-7-yloxyacetyl)-N[3]-arylureas have been synthesised. Six of them reduced the blood sugar upto 24% in rats at an oral dose of 250 mg/kg body weight.

RECENTLY, CS476, N[1]-[4-{2-(2,3-dihydrobenzo (b)furan-7-carboxamido) ethyl benzene sulphonyl] -N[3]-cyclohexylureas has been claimed[1,2,3], to be as potent a hypoglycemic agent as Glybenclamide[4]. Also, 4,5,6-trimethyl coumrin derivatives[5] were found to possess antidiabetic activity comparable to that of chlorpropamide[6]. It was, therefore, considered of interest to synthesise title compounds with a view to study the effect of introducing ureido group in both coumarone (benzofuran) and coumarin nuclei on their hypoglycemic activity.

α-Chloroacetyl-N-arylurea was refluxed with 2,3-diphenyl-6-hydroxy coumarone in dry acetone in the presence of anhydrous K_2CO_3 to give desired coumaronyloxyacetylurea. The same chloroacetylurea was also refluxed with 4-methyl-7-hydroxy coumarin under similar conditions to furnish corresponding coumarinyloxy acetylurea. The compounds, thus synthesised were characterized by their elemental analysis and I.R. spectra.

TABLE 1—N[1]-(2,3-DIPHENYL COUMARON-6-YLOXYACETYL)-N[3]-ARYLUREAS[+]



Compound No.	Ar	M.P. °C
1.	C_6H_5	178
2.	$2\text{-}CH_3C_6H_4$	218
3.	$3\text{-}CH_3C_6H_4$	233
4.	$4\text{-}CH_3C_6H_4$	240
5.	$2\text{-}OCH_3C_6H_4$	208
6.	$3\text{-}OCH_3C_6H_4$	211
7.	$4\text{-}OCH_3C_6H_4$	222
8.	$4\text{-}OC_2H_5C_6H_4$	204
9.	$2\text{-}ClC_6H_4$	258
10.	$4\text{-}ClC_6H_4$	280

All compounds analysed well for C, H and N.

[+] Yields ranged between 45-60%.

Compounds No. 1, 4, 6, 7, 8 and 10 showed characteristic bands at 3150-3250 cm^{-1} (-NH), 1640-1690 cm^{-1} (amide C=O) and 1160-1240 cm^{-1} (Ar-o-CH_3).

Experimental

All melting points are uncorrected. Infrared spectra were determined on a Perkin-Elmer 137 spectrophotometer in KBr. T.L.C. was carried out using kiesel gel G. coated glass plates of 2 mm thickness.

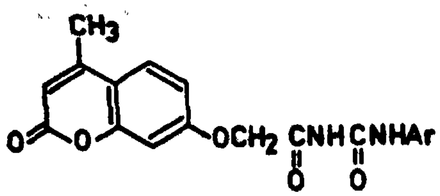
N[1]-(2,3-Diphenyl Coumaron-6-yloxyacetyl)-N[3]-arylureas :

A mixture of α-chloroacetyl-N-arylurea[7,8,9] (0.005 mole), 2,3-diphenyl-6-hydroxy coumarone[10] (0.005 mole), dry acetone (50 ml) and anhydrous K_2CO_3 (0.01 mole) was refluxed for 18 hours on a steam bath. The reaction mixture was evaporated to dryness and 100 ml of cold water was added to the dry mass with stirring. A solid so obtained was filtered and washed several times with cold water and recrystallised from ethanol. Compounds prepared are listed in Table 1.

N[1]-(4-Methyl Coumarin-7-yloxyacetyl)-N[3]-arylureas :

α-Chloroacetyl-N-arylurea (0.007 mole), 4-methyl-7-hydroxy coumarin[11] (0.007 mole), anhydrous K_2CO_3 (0.01 mole) and dry acetone (100 ml) were refluxed for 16 to 18 hours on a steam bath. Thereafter, the mixture was evaporated to complete dryness and water (100 ml) was added to it with shaking. The solid thus separated was filtered, washed several times with cold water and recrystallised from 90% ethanol. Compounds prepared are listed in Table 2.

TABLE 2—N^1-(4-METHYL COUMARIN-7-YLOXYACETYL)-N^3-ARYLUREAS+



Compound No.	Ar	M.P °C
11.	C_6H_5	198
12.	2-$CH_3C_6H_4$	224
13.	3-$CH_3C_6H_4$	212
14.	4-$CH_3C_6H_4$	262
15.	2-$OCH_3C_6H_4$	235
16.	3-$OCH_3C_6H_4$	218
17.	4-$OCH_3C_6H_4$	214
18.	4-$OC_2H_5C_6H_4$	210
19.	2-ClC_6H_4	214
20.	4-ClC_6H_4	225

All compounds analysed well for C, H and N.
+Yields ranged between 60-70%.
The I. R. spectra of the Compounds No. 12, 14, 16, 17, 18 and 20 showed characteristic bands at 3100-3200 cm^{-1} (-NH), 1710-1725 cm^{-1} (lactone C=O), 1690-1600 cm^{-1} (amide C=O) and 1220-1140 cm^{-1} (Ar-o-CH_2).

Pharmacology :

Six of the compounds (No. 4,7,8,14,17 and 18) were examined for their hypoglycemic activity, for which blood samples were drawn from the tail vein of fasted albino rats weighing between 200 and 250 gms and their glucose contents were estimated by Nelson Somogyi method[12]. The compounds under test were administered orally at single oral dose of 250 mg/kg body weight. Blood samples were again taken at intervals of 1,2 and 4 hours and their glucose contents were estimated. The average maximum reduction in blood sugar for the above compounds were 24,11,9,13,10 and 7% respectively. It appears that in both the coumarin and coumarone series the compound with Ar=*p*-Tolyl analogous to that present in a well known antidiabetic drug Tolbutamide had the highest hypoglycemic activity. It is also inferred that the introduction of ureido group in both coumarin and coumarone nuclei did not enhance the hypoglycemic activity to a significant extent.

Acknowledgement

We are indebted to Prof. S. S. Tiwari, Head, Department of Chemistry, Lucknow University for affording departmental facilities and Dr. Nitya Nand, Director, C.D.R.I., Lucknow for providing pharmacological data. Thanks are also due to S.C.S.T., U.P., Lucknow for the award of a Junior Research Fellowship to one of us (G.C.S.).

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 742-743

Synthesis and Cardiovascular Activity of Piperidyl Ethyl Indoles

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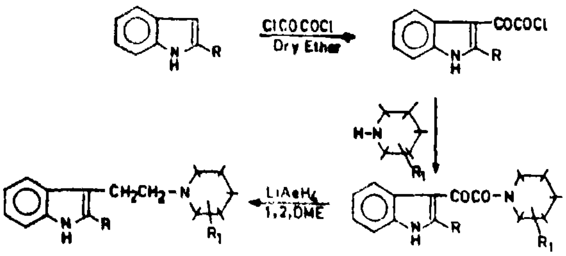
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Manuscript received 9 February 1979, revised 3 September 1979, accepted 9 January 1980

Some new 2-substituted-N-(substituted piperidyl) indole-3-yl-glyoxylamides and 2-substituted-3-[β-{N-(substituted piperidyl) }ethyl] indoles have been synthesized as possible cardiovasc ular agents by the condensation of different piperidines with indole glyoxylylchloride followed by reduction with lithium aluminium hydride in anhydrous dimethoxyethane.

INDOLE derivatives have been reported to possess marked antihypertensive activity[1-6]. Several benzamidopiperidyl ethyl indoles have been reported as cardiovascular agents[7,8]. Recently indoramin-3-2-(4-benzamidopeprid-1-yl)-ethyl indole has been found to possess sustained hypotensive, antihistaminic and adrenoceptor blocking activities and is used clinically in man[9-12].

With a view to study the effect of other functional variants on hypotensive activity we have synthesized a series of 2-substituted-N-(substituted piperidyl) indole-3-glyoxylamides and 2-substituted-3-[β-{N-(substituted piperidyl)} ethyl] indoles and evaluated them for their cardiovascular activity. The compounds were synthesized according to the route given below :



II   I

Experimental

Melting points were taken in open capillary tubes and are uncorrected. Compounds were routinely checked for their homogeneity by TLC on Silica Gel G. Infrared spectra (νmax in cm^{-1}) was recorded on Perkin Elmer infracord 137. Substituted indoles were prepared according to known procedures[13,14]. Substituted indoleglyoxylylchlorides were prepared following the reported methods[15,16].

2-Substituted-N'-(Substituted piperidyl)- indole- 3- yl glyoxylamides :

To substituted indoleglyoxylylchloride (0.01 mole) in dry benzene (50 ml), substituted piperidine (0.01 mole) was added slowly. The reaction mixture was refluxed on a water bath for 8 hrs and the benzene distilled off. The residue was washed with pet ether and recrystallized from DMF-water. The m.p.s, yields and other analytical data of the synthesized compounds are given in Table 1. Compounds No. 2, 6 and 7 in table 1 showed characteristic bands of—NH stretching vibration (3200 cm^{-1}) and C=O stretching vibration (1660 cm^{-1}) in the infra red spectrum.

2-Substituted-3-[β{-N-Substituted piperidyl)} ethyl] indoles :

To a stirred mixture of $LiAlH_4$ (1 gm) in 1.2-dimethoxy ethane (dry, 50 ml) was added 2-substituted piperidyl) indole 3-yl glyoxylamide (0.005 mole) in small portions at such a rate, as to keep the reaction temperature below 35°. The reaction mixture was refluxed for 18 hours, cooled to-5°. Excess $LiAlH_4$ was decomposed by dropwise addition of H_2O, the inorganic material was filtered off and the filtrate evaporated to a solid It was recrystallized with appropriate solvent. The melting points, recrystallisation solvents and other analytical data are given in Table 2. Compounds No. 12, 16 and 17 in Table 2 showed the characteristic bands of-NH stretching vibration (3300 cm^{-1}) in the infra red spectrum, the C=O stretching band was completely absent.

Biological studies :

Dogs were anaesthetized with pentobarbitone sodium (30 mg/kg) maintained on positive pressure

* Part of this work will be incorporated in the Ph.D. thesis of Jagdish C. Agarwal.
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TABLE 1—2-SUBSTITUTED-N'-(SUBSTITUTED PIPERIDYL)-INDOLE-3-YL GLYOXYLAMIDES(I)

Sl. No.	R	R_1	M.P. °C	Yield %	Molecular formula	% Nitrogen Calcd.	% Nitrogen Found	Dose mg/kg IVI	%Change in B. P. (a)	Effect of CO and NA responses
1.	H	4-OH,4-C_6H_5	180	70	$C_{21}H_{20}N_2O_3$	8.04	8.01	3	-	No effect
2.	H	2-CH_3	165	75	$C_{16}H_{18}N_2O_2$	10.37	10.32	3	-9.1	"
3.	H	3-CH_3	160	80	$C_{16}H_{18}N_2O_2$	10.37	10.41	2	-	"
4.	H	3-OH	178	65	$C_{15}H_{16}N_2O_3$	10.29	10.25	2	-	"
5.	CH_3	2-CH_3	185	70	$C_{17}H_{20}N_2O_2$	9.85	9.83	2	-	"
6.	CH_3	3-CH_3	181	75	$C_{17}H_{20}N_2O_2$	9.85	9.89	2	-	"
7.	CH_3	3-OH	192	65	$C_{16}H_{18}N_2O_3$	9.79	9.84	2	-	"
8.	CH_3	4-OH,4-C_6H_5	178	65	$C_{22}H_{22}N_2O_3$	7.73	7.79	2	-	"
9.	C_6H_5	4-OH,4-C_6H_5	166	80	$C_{27}H_{24}N_2O_3$	6.60	6.68	3	-	"
10.	C_6H_5	2-CH_3	184	75	$C_{22}H_{22}N_2O_2$	8.09	8.02	2	-	"

(a) % change in blood pressure as compared to control. —indicates decrease in blood pressure
+ indicates increase in blood pressure

TABLE 2—2-SUBSTITUTED-3-[β-{N'-(SUBSTITUTED PIPERIDYL)} ETHYL] INDOLE(II)

Sl. No.	R	R_1	M.P. °C	Yield %	Recryst. solvent	Molecular formula	% Nitrogen Calcd.	% Nitrogen Found	Dose mg/kg IVI	% Change in B. P. (b)	Effect of CO and NA responses
11.	H	4-OH,4-C_6H_5	110	35	E-C	$C_{21}H_{24}N_2O$	8.75	8.72	2	-	No effect
12.	H	2-CH_3	124	30	A	$C_{16}H_{22}N_2$	11.57	11.51	3	-13.2	"
13.	H	3-CH_3	120	40	A	$C_{16}H_{22}N_2$	11.57	11.59	3	-	"
14.	H	3-OH	145	35	A	$C_{15}H_{20}N_2O$	11.48	11.42	2	-	"
15.	CH_3	2-CH_3	154	30	E-C	$C_{17}H_{24}N_2$	10.80	10.80	2	-	"
16.	CH_3	3-CH_3	128	35	E-C	$C_{17}H_{24}N_2$	10.82	10.88	2	+22.5	"
17.	CH_3	3-OH	136	30	E-C	$C_{16}H_{22}N_2O$	10.74	10.71	2	+16.8	"
18.	CH_3	4-OH,4-C_6H_5	120	35	E-C	$C_{22}H_{26}N_2O$	8.38	8 32	2	-	"
19.	C_6H_5	4-OH,4-C_6H_5	142	30	C	$C_{27}H_{28}N_2O$	7.14	7.14	3	- 19.07	"
20.	C_6H_5	2-CH_3	122	40	B	$C_{22}H_{26}N_2$	8.84	8.80	3	-	"

(a) A-Ethanol, B-Methanol, C-Acetone, E-Ether
(b) % change in blood pressure as compared to control —indicates decrease in blood pressure
+indicates increase in blood pressure

artificial respiration. The blood pressure (B. P.) was recorded from the common carotid artery through a mercury manometer on kymograph paper. Drugs were administered through cannulated right femoral vein. The effect of compounds was studied on resting B. P. and on pressor responses evoked either by carotid occlusion (CO) for 10-30 seconds or by 1-2 μg/kg of noradrenaline (NA) given intravenously.

Results and Discussion

The cardiovascular effects of this group of compounds are summarised in Table 1 and 2. Out of 20 compounds tested, only compounds 2, 12 and 19 elicited a mild hypotensive activity without affecting the CO and NA response. Compounds 16 and 17 on the other hand induced a short lasting hypertensive response. The remaining fifteen compounds failed to exhibit any cardiovascular effects in the doses tested.

Acknowledgement

The authors wish to express their thanks to Dr. V. S. Misra, Reader, Chemistry Department, Lucknow University, for his advice and encouragement.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 744-745

Optically Active Thiolesters from S–(+)–3-Methylcaproic Acid by Arndt-Eistert Synthesis

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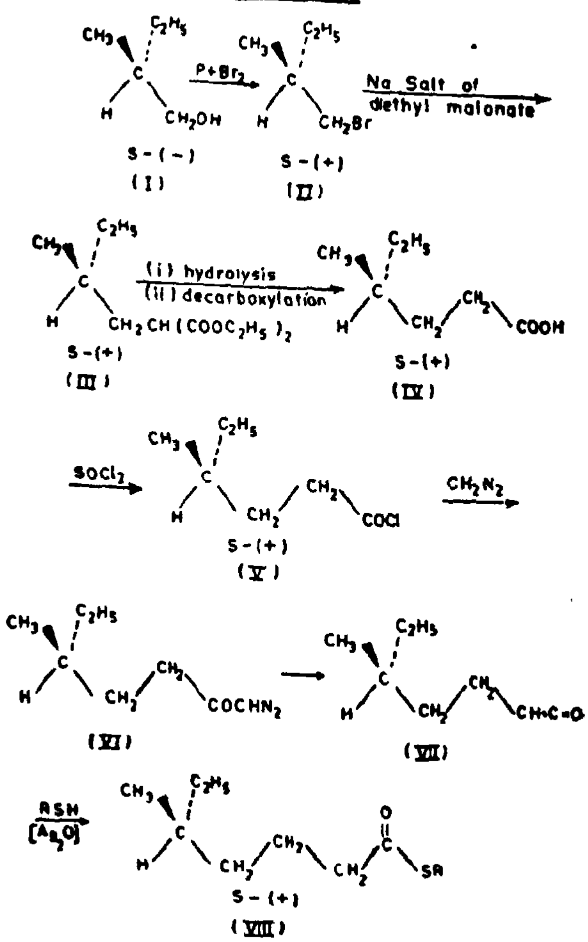
Manuscript received 29 August 1979, revised 3 March 1980, accepted 9 April 1980

For the first time by Arndt-Eistert synthesis the thiolesters are prepared using mercaptans. The various alkyl mercaptans react with diazoketone prepared from S–(+)–3-methylcaproyl chloride yield a series of higher homologous optically active thiolesters of the type, $CH_3CH_2.\overset{*}{C}H(CH_3).CH_2CH_2CH_2COSR$, where R = *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl, *n* hexyl, *n*-heptyl and *n*-octyl. The optical rotation and infrared spectra of these thiolesters have been studied.

THE synthesis of aliphatic and aromatic thiolesters have been reported earlier[1-8] by esterification of acids with mercaptans just like alcohols. Mischler[8] found that aromatic and aliphatic acid chlorides give satisfactory results with mercaptans and aqueous alkali. Vasi and co-workers[7-10] have prepared various optically active aliphatic thiolester from optically active S–(–)–2-methyl butan-1–ol.

It is likely that Arndt-Eistert synthesis can be carried out with bivalent sulphur containing compound, similar to that of the oxygen containing alcohol analogs. In view of this the present work is carried out to synthesise optically active thiolesters for the first time by Arndt-Eistert synthesis, where alkyl mercaptans are used instead of alcohols. S–(+)-2–methyl butan-1-ol (I), α_D^{32} -4.62, on bromination with red phosphorous and bromine resulted in S–(+)–2-methyl-1-bromobutane II), α_D^{32} +1.69. It was condensed with sodium salt of diethylmalonate to form optically active diethyl S–(+)–2-methyl-1-butyl malonate (III), α_D^{32} +4.96, which on hydrolysis with alkali and then on decarboxylation by heating with sulphuric acid gave S–(+)–3-methylcaproic acid (IV), α_D^{32} +4.75. On treatment with thionyl chloride acid gave S–(+)–3-methylcaproyl chloride (V), α_D^{32} +4.98. The diazomethane prepared from nitroso-methyl urea reacted with S–(+)–3-methylcaproyl chloride gave diazoketone(VI) and then ketone (VII). Various alkyl mercaptans reacted with ketene in presence of silver oxide gave optically active thiolesters (VIII).

REACTIONS



R = VARIOUS ALKYL GROUPS

Experimental

S–(+)–2-Methyl-1-bromobutane :

It was prepared by bromination of S-(–)-2-methyl butane-1-ol α_D^{32} –4.62, (320 g.), with red phosphorous (20.7 g.) and bromine (266 g., 86.1 ml). The

resulting S—(+)—2-methyl-1-bromobutane distilled at 116-118° ; yield 57.3%.

α_D^{32} +1.69 ; d_4^{32} 1.253 ; n^{32} 1.436

TABLE 1—OPTICALLY ACTIVE THIOLESTERS OT THE TYPE

$CH_3CH_2.\overset{*}{C}H(CH_3).CH_2CH_2CH_2COSR$

No.	Name	R	Yield %	B.P. °C	Specific Rotation α_D^{30}	d_4^{30}	n^{30}	C=O stretching vibrations R′-C(=O)-S-R	% Sulphur Found	% Sulphur Calc.
1.	S—(+)—*n*-Propyl-4-methyl thiolenanthate	*n*-Propyl	48.0	185-187	+1.98	0.8789	1.427	1730 cm⁻¹ (5.78 μ)	15.86	15.84
2.	S—(+)—Isopropyl-4-methyl thiolenanthate	Iso-propyl	45.0	205-207	+4.28	0.8752	1.425	1739 cm⁻¹ (5.75 μ)	15.88	15.84
3.	S—(+)—*n*-Butyl-4-methyl thiolenanthate	*n*-Butyl	49.0	217-219	+4.34	0.8792	1.427	1730 cm⁻¹ (5.78 μ)	14.76	14.81
4.	S—(+)-Isobutyl-4-methyl thiolenanthate	Iso-butyl	42.0	183-185	+2.45	0.8769	1.426	1736 cm⁻¹ (5.76 μ)	14.79	14.81
5.	S—(+)—*n*-Amyl-4-methyl thiolenanthate	*n*-Amyl	50.0	217-219	+4.53	0.8814	1.429	1739 cm⁻¹ (5.75 μ)	13.93	13.91
6.	S—(+)—*n*-Hexyl-4-methyl thiolenanthate	*n*-Hexyl	40.0	202-204	+4.88	0.8800	1.428	1736 cm⁻¹ (5.76 μ)	13.08	13.11
7.	S—(+)-*n*-Heptyl-4-methyl thiolenanthate	*n*-Heptyl	48.0	196-198	+3.58	0.8991	1.425	1736 cm⁻¹ (5.76 μ)	12.39	12.40
8.	S—(+)-*n*-Octyl-4-methyl thiolenanthate	*n*-Octyl	49.0	218-220	+2.08	0.8920	1.427	1739 cm⁻¹ (5.75 μ)	11.80	11.76

S—(+)—3-Methylcaproic acid :

S—(+)—2-Methyl-1-bromobutane, α_D^{32} + 1.69, (116 g.), was condensed with sodium salt of diethyl malonate ; prepared from sodium (19.8 g.), absolute ethanol (350 ml) and diethyl malonate (126 g., 117 ml). Diethyl S—(+)—2-methyl-1-butyl malonate, α_D^{32} +4.96, was hydrolysed with a hot solution of potassium hydroxide (47.5 g) in water (47.5 ml), and then decarboxylated by heating with sulphuric acid (44 ml) in water (110 ml) for 4 hrs gave S—(+)—3-methylcaproic acid. It was purified by distillation at 210° ; yield 70%.

α_D^{32} +4.75 ; d_4^{32} 0.9679 ; n^{32} 1.433.

(Found by titration with 0.1 *N* sodium hydroxide, MW 131.5 ; $C_7H_{14}O_2$ requires MW 130.0).

S—(+)—3-Methylcaproyl chloride :

S—(+)—3-Methylcaproic acid (130 g., 1.0 *M*) was added dropwise during 1 hr to redistilled thionyl chloride (180 g., 1.5 *M*) at 10°. It was then refluxed for 1 hr and excess of thionyl chloride was distilled off. The residual S—(+)—3-methylcaproyl chloride was purified by distillation at 168-170° ; yield 57%.

α_D^{32} + 4.98 ; d_4^{32} 0.9675 ; n^{32} 1.432.

General method for the preparation of optically active thiolesters :

S—(+)—3-Methylcaproyl chloride (29.7 g.) was added to a solution of diazomethane[11,12] in 500 ml ether. The reaction mixture was allowed to stand at 20-25° for 3 to 4 hrs. The ether was removed under reduced pressure, and to the residual diazoketone, alkyl mercaptan (0.2 *M*) and silver oxide (2.0 g.) were added. The contents were refluxed for 2 hours on water bath. The reaction mixture was then cooled, filtered, dried and distilled to obtain optically active thiolester.

Acknowledgement

We are thankful to Government of Gujarat for Research Fellowship to one of us (NTN) and to Gujarat University for research facilities.

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Notes

Some Observations on Nickel(II) Complexes of Hydroxyaldimino Amino Acids

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Manuscript received 26 November 1979, accepted 22 December 1979

During our studies on nickel(II) mixed chelates containing salicylideneamino acids and dipyridyl (or *o*-phenanthroline)[1,2] as we had occasion to use some nickel(II) salicylideneamino acid complexes as reported by Ray and Mukherjee[3]. The complex $[Ni(salglyH)_2]$[3] [$(salglyH)_2$ = salicylidene glycin] appears to date the only *bis* salicylideneamino acidato) nickel(II) chelate. These authors have also reported an apparently four-coordinated monomeric [Ni(sal α-alan) (OH_2)] (sal α-alanH_2 = salicylidene α-alanine) and a five-coordinated mixed chelate [Ni(α-alanH) (sal-α-alan)] (α-alanH = α-alanine)[3]. Structures of these chelates had not been adequately supported by spectral and thermal data. In this note we have endeavoured to establish the identities and develop authentic synthetic procedures for some salicylidene amino acid chelates of nickel(II).

Experimental

Bis (salicylaldehydato) diaquo nickel(II)[4] and *bis* (aminoacidato) diaquo nickel(II)[5] were prepared by published procedures.

Bis (salicylideneglycinato) nickel(II) :

Method A : $[Ni(OH_2)_2(sal)_2]$ (salH = salicylaldehyde ; 0.003 mol) and glycine (glyH ; 0.006 mol) were taken in 1 : 1 water-ethanol (20 ml) and refluxed for five minutes. The solution was filtered and the filtrate cooled in a refrigerator overnight. Violetish blue crystals were dried in air.

Method B : $[Ni(OH_2)_2(gly)_2]$ (0.002 mol) and salicylaldehyde (0.004 mol) in ethanol (20 ml) were allowed to reflux for one hour. The precipitated compound was collected, triturated with water (10 ml) on a steam bath for five minutes, filtered and finally dried in air. The substance is insoluble in all common solvents.

Both the methods gave satisfactory analyses for $[Ni(salglyH)_2]$ (Found : H_2O, 2.1 ; Ni, 13.7 ; N, 6.4 ; Calc : H_2O, 2.1 ; Ni, 13.9 ; N, 6.6 percent) $0.5H_2O$.

Bis(salicylidene α-alaninato) nickel(II) :

Method A : $[Ni(H_2O)_2(sal)_2]$ (0.002 mol) and α-alanine (0.004 mol) were taken in ethanol (40 ml) and refluxed for ten minutes. The solution was filtered hot and the filtrate was allowed to stand for two hours. The blue needle shaped crystals were collected and dried in air. On allowing to stand overnight a mixture of blue and green crystals was obtained.

Method B : $[Ni(H_2O)_2$(α-alan)$_2]$ (0.002 mol) and salicylaldehyde (0.004 mol) were refluxed in ethanol (25 ml) for fifteen minutes. After filtrtation the green solution was allowed to stand for wo hours. Blue crystals were collected and dried in air. On standing for a longer period a mixture of blue and green crystals were obtained. The compound is insoluble in all common solvents.

Both the methods provided satisfactory analyses for [Ni(sal α-alanH)$_2$]H_2O. (Found : H_2O, 3.8 ; Ni, 12.4 ; N, 5.9 ; Calc : H_2O, 3.9 ; Ni, 12.5 ; N, 6.1 percent).

μ-Bis(salicylidene α-alaninato) Tetraaquodinickel(II) :

Method A : $[Ni(H_2O)_2(sal)_2]$ (0.003 mole) and α-alanine (0.003 mol) in water (80 ml) were digested on a steam bath for one hour. A small amount of unreacted $[Ni(H_2O)_2(sal)_2]$ was removed by filtration, the filtrate concentrated to 20 ml and left overnight in a refrigerator. The green crystals were collected, washed with cold water and ethanol and finally dried in air.

Method B : $[Ni(H_2O)_2$ (α-alan)$_2]$ (0.003 mol) was dissolved in water (25 ml) and to this salicylaldehyde (0.003 mol) in ethanol (10 ml) was added dropwise with stirring. The solution was then cooled in ice for half an hour and the green crystals were collected and dried as in method A.

Both the methods gave good analytical results for $[Ni(H_2O)_2$ (sal α-alan)$]_2$. Found : H_2O (thermogravimetric) 11.5 ; Ni, 20.2 ; N, 20.5 ; Calc : H_2O, 12.6 ; Ni, 20.5 ; N, 4.9 percent).

Results and Discussion

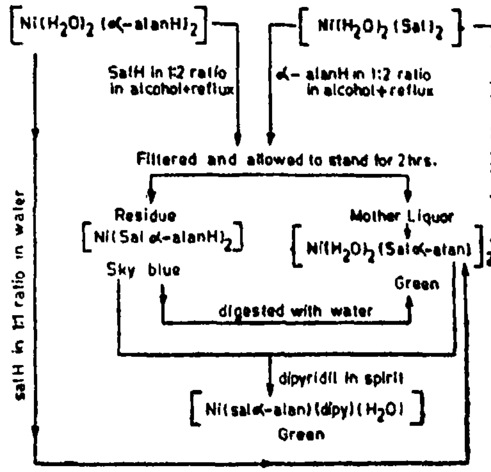
Bis(salicylideneglycinato) nickel(II) : This compound was originally prepared by Ray and Mukherjee by the reaction of aqueous glycine with an alcoholic suspension of *bis*(salicylaldehydato) diaquo nickel(II)[3]. We now find that this synthesis can be carried out in an entirely aqueous medium. We have also been able to produce the same substance by a template reaction between salicylaldehyde and *bis*(glycinato) diaquo nickel(II) in an entirely aqueous medium. Successful preparation of the complex in an entirely aqueous medium is certainly due to the thermodynamic stability[6] of the complex, arising out of chelation, which resists any nucleophilic attack by H_2O on the azomethine carbon of the Schiff base. Both the preparations provide the expected magnetic moment (~ 3.0 B.M.). The solid state electronic spectrum reveals to absorption bands at 11.50 kK

and 17.50 kK. These are assigned to well known transitions[7]. $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ respectively in octahedral symmetry. The ν_2/ν_1 ratio 1.52 falls within the range of pseudooctahedral nickel(II) chelates[8]. The 10 D_q (ν_1) value of 11.5 kK indicates a good ligand field about nickel(II). The third transition is not discernible.

Bis(salicylidene ∝-alaninato) nickel(II) and μ-bis salicylidene ∝-alaninato) tetraaquo nickel(II): Ray and Mukherjee obtained their (alleged) green coloured [Ni(H_2O) (sal ∝-alan)] (with an apparent C.N.4) by the reaction of *[Ni(H_2O)$_2$(sal)$_2$]* with an excess of ∝-alanine (1:2.3) in aqueous solution. Their mixed complex [Ni-(∝-alanH) (sal ∝-alan)] (with an apparent C.N.5) was obtained by the interaction of the same two reactants in alcoholic solution using a ratio 1:3.5.

Besides reproducing Ray and Mukherjee's method we have also obtained their green coloured product by (i) the reaction of *bis*(∝-alaninato) diaquo nickel(II) with salicylaldehyde in the ratio 1 : 1 and (ii) the reaction of *bis*(salicylaldehydato) nickel(II) with ∝-alanine in aqueous medium again in the ratio 1 : 1. Our analyses point to the empirical formula [Ni(H_2O)$_2$(sal ∝-alan)] rather than to [Ni(H_2O) (sal ∝-alan)]. Our product compares well with the compound reported by Theriot[9] via reaction of aqueous nickel(II) acetate with aqueous alcoholic solution of ∝-alanine and salicylaldehyde. The magnetic moments of these preparations are in the expected range (3.13-3.15 B.M.) for pseudooctahedral nickel(II). The ν_1 and ν_2 bands in the mull spectrum appear at 10.60 kK and 15.6 kK. The ν_2/ν_1 ratio of 1.42 is also indicative of a pseudooctahedral structure. The ν_1 and ν_2 bands (11.24 kK and 16.45 kK) as reported by Theriot[9] seem to be erroneous as the ν_1 band indicates too high a 10 Dq for a complex with an [$NiNO_5$] chromophore. Thus for the green complex [Ni(H_2O) (sal ∝-alan)] of Ray and Mukherjee we suggest a *μ-bis*(salicylidene ∝-alaninato) tetraaquodi nickel(II) : [Ni(H_2O)$_2$(sal ∝-alan)]$_2$ with the H_2O molecules occupying *trans* apical sites of the two pseudooctahedral nickel(II) [c f. the structures of nickel(II)[9], cobalt(II)[10] and manganese(II)[11] chelates of similar hydroxy aldiminoamino acids]. A thermogravimetic study shows loss of two H_2O molecules per nickel over the temperature range 50-200°.

We have not been able to reproduce the synthesis of the alleged five-coordinate [Ni(∝-alanH) (sal ∝-alan)], all variations of which led to the blue coloured [Ni(sal ∝-alanH)$_2$] H_2O. The mixed chelate formulation (with a C.N. 5 would require a sharp NH stretch (due to ∝-alanH) and a rich electronic spectrum (with a characteristic band around 7 kK)[12]. The infrared spectrum of the monohydrate [Ni(sal ∝-alanH)$_2$]H_2O records only a weak broad absorpion around 3400 cm^{-1} which is evidently due to the lattice water that it carries. The solid state spectrum to the complex reveals only two bands : ν_1 at 11.49 kK and ν_2 at 18.01 kK but none at lower energy. Again ν_2/ν_1 ratio 1.57 is indicative of a pseudooctahedral stereochemistry.



Scheme 1: Formation and reactions of salicylidene-∝-alanine complex of nickel (II).

It is interest to note that digestion of [Ni(sal ∝-alanH)$_2$]H_2O with hot water slowly converts it to the green coloured [Ni(H_2O)$_2$(sal ∝-alan)]$_2$ indicating partial nucleophilic attack on one of the two C=N bonds. Scheme I gives the formation and some reactions of salicylidene ∝-alanine complexes of nickel(II).

Acknowledgement

We thank CSIR for financial assistance.

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J. INDIAN CHEM. SOC., VOL. LVII, JULY 1980

Palladium(II) Chelates of α-Oximinoacetoacetarylamide Thiosemicarbazones

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Manuscript received 18 June 1979, revised 11 December 1979, accepted 23 April 1980

IN continuation of our previous work[1-7], we describe the preparation and characterisation of Pd(II) chelates of α-oximinoacetoacetarylamide thiosemicarbazones in the present paper.

Experimental

Preparation of the Pd(II) chelates of the α-oximinoacetoacetanilide thiosemicarbazone :

10 ml aqueous solution of Pd(II) chloride (0.05*M*) was gradually added to 25 ml alcoholic solution (2%) of α-oximinoacetoacetanilide thiosemicarbazone and acidified with dilute HCl. The mixture was diluted to about 100 ml with distilled water and digested on waterbath for half an hour. The red precipitates separated were filtered, washed with hot water and aqueous ethanol (1 : 1), and dried in an oven at 110°. The Pd(II) chelates of the other α-oximinoacetoacetarylamide thiosemicarbazones of the series were prepared in the similar manner. The m. p., colour, elemental analysis and composition of the Pd(II) chelates are given in Table. The infrared spectra of the ligands and chelates were recorded in KBr pellets.

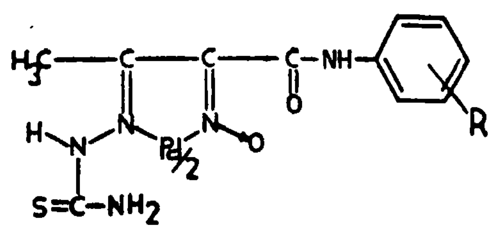
Results and Discussion

Infrared spectra :

An assignment of the important infrared absorption bands is based on the study of infrared spectra of the free ligands and their chelates. The band at 2833-2890 cm^{-1} appears in the ligands but does not appear in the chelates. This indicates the presence of intramolecular H-bond in the ligands[8]. The absence of this band in the chelates is the indication of the replacement of hydrogen of oximino group by metal ion. The fact that νNO shifts from 952-966 cm^{-1} in the free ligands to 1160-1180 cm^{-1} in the chelates indicates that the coordination of the ligand to the metal is through N and not through O of oximino group and the chelates contain the nitrone (N→O) type of linkage which is known to absorb at about 1200 cm^{-1} as a very strong band[9]. The shift of νNO from about 1000 cm^{-1} in ligand to about 1200 cm^{-1} shows the nitronic type of linkage in many oxime complexes[10-12]. The lowering of the νC=N stretching frequency from 1600-1610 cm^{-1} in the ligands to 1590-1595 cm^{-1} in the chelates is indicative of 1-N coordination of thiosemicarbazide moiety. The νN-N band around 1030-1045 cm^{-1} in the ligands shifts to the higher frequency in the chelates. The magnitude of this positive shift (15-30 cm^{-1}) indicates the monodentate linkage of N-N residue[13]. The presence of C=S bands at 826-840 cm^{-1} and 1050-1083 cm^{-1} in the free ligands as well as in chelates suggest that C=S group is not involved in the coordination of metal[14]. Further more it indicates that the ligands act as bidentate and not as tridentate. The infrared spectra of the ligands and chelates reveal bands around 3300, 3100 and 3460 cm^{-1}, indicating secondary association, primary association and free N—H vibrations of amides respectively[15]. The strong bands in the ligands and chelates around 1620 and 1660 cm^{-1}, 1540 cm^{-1} and 1300 cm^{-1} are attributed to amide I, II and III bands respectively[15].

From infrared spectra and metal : ligand ratio (1 : 2) of the chelates, it is concluded that α-oximinoacetoacetarylamide thiosemicarbazones act as bidentate ligands.

TABLE—PALLADIUM CHELATES OF α-OXIMINOACETOACETARYLAMIDE THIOSEMICARBAZONES



No.	R	Composition	Colour	m.p.°C (decomp.)	% Palladium Found	% Palladium Requd.	% Nitrogen Found	% Nitrogen Requd.
1.	H	$C_{22}H_{24}N_{10}O_4S_2Pd$	Red	178	16 16	16.10	21.0	21.12
2.	*o*-CH_3	$C_{24}H_{28}N_{10}O_4S_2Pd$	Orange red	208	15.32	15.45	20.18	20.27
3.	*p*-CH_3	$C_{24}H_{28}N_{10}O_4S_2Pd$	Deep red	200	15.39	15.45	20.20	20.27
4.	*o*-Cl	$C_{22}H_{22}N_{10}O_4S_2Cl_2Pd$	Deep red	360	14.52	14.58	19.09	19.14
5.	*m*-Cl	$C_{22}H_{22}N_{10}O_4S_2Cl_2Pd$	Orange	207	14.55	14.58	19.20	19.14
6.	*p*-Cl	$C_{22}H_{22}N_{10}O_4S_2Cl_2Pd$	Red	210	14.50	14.58	19.10	19.14
7.	*o*-OCH_3	$C_{24}H_{28}N_{10}O_6S_2Pd$	Red	195	14.69	14.77	19 28	19.37
8.	*p*-OCH_3	$C_{24}H_{28}N_{10}O_6S_2Pd$	Red	222	14.80	14.77	19.27	19.37
9.	2,4-$(CH_3)_2$	$C_{26}H_{32}N_{10}O_4S_2Pd$	Deep red	286	14.78	14.84	19.42	19.48
10.	2,4-$(OCH_3)_2$	$C_{26}H_{32}N_{10}O_8S_2Pd$	Orange	232	13.70	13.63	17.78	17.89
11.	*p*-OC_2H_5	$C_{26}H_{32}N_{10}O_6S_2Pd$	Orange red	215	14.17	14.21	18.78	18.65

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Acknowledgement

The authors wish to express their sincere thanks to Prof. B. N. Mankad for the keen interest shown in the work.

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Physical Properties of Iron Lauryl Sulphate and Laurate Solutions in 1-butanol

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Manuscript received 13 November 1979, accepted 18 March 1980

A number of workers[1-5] have reported a considerable information about the physical properties of soaps in 1-butanol. In this note a comparative study of these properties of iron lauryl sulphate and laurate has been carried out.

Experimental

The chemicals were purified and the compounds prepared by the method reported earlier[8]. Excess of solid compounds and 1-butanol were equilibrated at different temperatures by thorough stirring. The thermostat bath was controlled to within $\pm 0.5°$. Clear supernatant saturated solution was taken only when the equilibrium was attained (after 1-2 hrs) with pipette, evaporated, dried and weighed. The apparatus and procedure of conductivity and viscosity measurements were the same as described elsewhere[6,7].

Results and Discussion

Solubility : Solubility of compounds (Table 1) increases with increase in temperature. It is observed that the solubility of lauryl sulphate increases very slowly with increase in temperature. This behaviour is also found for laurate at low temperatures but an abrupt increase in solubility occurs at higher temperatures. The low solubility is due to its molecular state and formation of micelles in solutions increases the solubility abruptly.

The plots of log S vs 1/T are characterised by an intersection of two straight lines at a point corresponding to Krafft point i.e., 45° and 50° for lauryl sulphate and laurate respectively. The apparent heat of solution, ΔH_{sol} has been calculated by the following relationship

$$\Delta H_{sol} = RT^2 \left[\frac{d \ln S}{dT} \right] \quad \dots \quad (i)$$

where S is the solubility in moles $litre^{-1}$ and other terms have their usual significances. The values of ΔH_{sol} below and above Krafft point are 11.44, 0.71 and 2.29, 0.17 Kcals $mole^{-1}$ respectively for laurate and lauryl sulphate.

Conductivity : Specific conductivity, k of solutions increases with increasing concentration at different temperatures. The plots (Fig. 1) of k vs C are characterised by an intersection of two straight lines at a definite concentration (Table 1) indicating CMC for laurate. However, the plots of lauryl sulphate are non-linear with concentration below CMC. The CMC value of lauryl sulphate solution increases with rise in temperature whereas the value for laurate is independent of temperature.

Table 1—Values of Solubility, CMC and Constants A and B of Iron Compounds in 1-Butanol at Temperatures (35-50°)

	Lauryl sulphate				Laurate			
Temp. in °C	Solubility (g/100 g)	CMC (moles $litre^{-1}$)	A	B	Solubility (g/100 g)	CMC (moles $litre^{-1}$)	A	B
35	2.90	0.006	1.71	0.48	1.41	0.008	1.46	0.26
40	2.92	0 007	1.78	0.45	1.55	0.008	1.40	0.29
45	3.05	0.008	1.86	0.43	2.51	0.008	1.64	0.23
50	3.08	0.010	1.92	0.41	3.39	0.008	1.36	0.30
55	3.10				3.65			
60	3.13				3.86			

The molecular conductivity of soap solutions decreases as the concentration of solution increases. The plots of λ vs $C^{\frac{1}{2}}$ are concave curves which shows the weak electrolyte behaviour of the soaps.

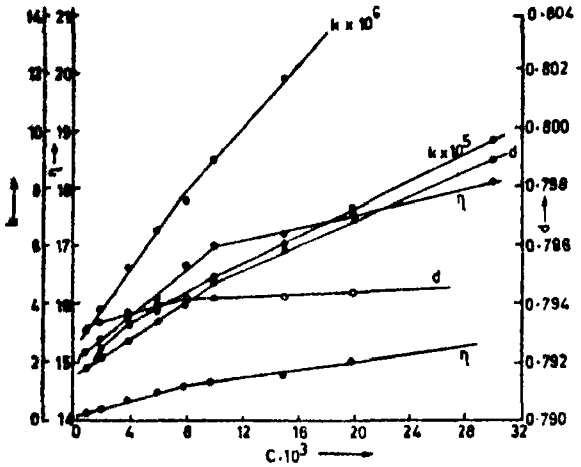


Fig. 1. Plots of specific conductivity, K(ohm^{-1} cm^{-1}) viscosity, η (millipvise) and density, d(g ml^{-1}) of iron compounds in 1—butanol at 50°.
O Laurate, ● Lauryl Sulphate.

The conductivity behaviour of compounds can be represented by following relationship :

$$\log \lambda = A + B \log C \qquad \text{... (i)}$$

where A and B are constants.

The values of A and B are given in Table 1. It is evident from the data of iron lauryl sulphate that the value of A increases but B remains constant with rise in temperature. These constants show irregular variation with increasing temperature in laurate and are lower than the other compounds. This irregular variation of constant B indicates that the CMC of iron laurate is affected by temperature. Such behaviour has also been observed[8] in iron caprylate and caproate in 1-butanol.

Since these compounds behave as an electrolyte in dilute solution, an expression[2] for their dissociation can be derived :

$$C^3 \lambda^3 = \frac{K \lambda_\infty^4}{27\lambda} - \frac{K\lambda_\infty^3}{27}$$

where K and λ_∞ are dissociation constant and molecular conductivity at infinite dilution, respectively. The plots of $C^3 \lambda^3$ vs $1/\lambda$ are linear below CMC and the equation fails above this concentration. The values of K and λ_∞ have been obtained from the intercepts and slopes of the plots and are recorded in Table 2. The dissociation constant of iron lauryl sulphate decreases with increasing temperature and are much lower than the corresponding values of iron laurate.

Molecular conductivity at infinite dilution, λ_∞ of iron lauryl sulphate increases with increasing temperature. This may be due to the decrease in viscosity of the solvent. The rise in temperature causes an increase in ionic mobility despite the fact that the addition of compound enhances the viscosity of the solvent. The values of λ_∞ of iron lauryl sulphate are higher than that of iron laurate. The results confirm that micellar aggregation is affected by temperature change.

Viscosity : The plots (Fig. 1) of viscosity vs concentration of the compounds are characterised by an intersection of two straight lines at CMC. The CMC values are the same as observed by conductivity measurements. Similar results are also obtained from density-concentration plots (Fig. 1).

Viscosity data has been interpreted with the aid of Vand[8] and Moulik[9] equations. These equations are found valid only in a limited range of concentration above CMC (Table 3). The parameters i. e., molar volume in litre mole^{-1}, $\bar{V}$, interaction coefficient, Q and Moulik's constants M and K' have been evaluated. Constant K' shows a reverse trend

TABLE 2—VALUES OF DISSOCIATION CONSTANT, K AND MOLECULAR CONDUCTANCE AT INFINITE DILUTION, λ_∞ OF IRON COMPOUNDS IN 1-BUTANOL AT TEMPERATURES (35-50°)

Temp. in °C	Lauryl sulphate $K \times 10^7$	λ_∞	Laurate $K \times 10^6$	λ_∞
35	7.63	9.60	3.27	1.87
40	4.08	11.67	6.59	1.60
45	1.05	16.66	0.39	2.62
50	0.32	23.75	7.41	1.45

TABLE 3—VISCOSITY PARAMETERS OF IRON COMPOUNDS IN 1-BUTANOL AT TEMPERATURES (35-50°)

Temp. in °C	Tested conc. range (moles litre^{-1})	Valid conc. range (moles litre^{-1})	$\bar{V}$	-Q	M	K'
			Lauryl sulphate			
35	0.001-.030	0.006-.030	3.91	12.77	1.11	125
40	.001-.030	.006-.030	10.14	12.17	1.23	138
45	.001-.030	.008-.030	15.66	9.89	1.33	200
50	.001-.030	.010-.030	31.32	7.36	1.53	212
			Laurate			
35	0.001-.020	0.008-.020	1.52	16.44	1.052	140
40	.001-.020	.008-.020	2.30	18.66	1.067	150
45	.001-.020	.006-.020	1.24	12.06	1.041	210
50	.001-.020	.006-.020	4.51	21.05	1.099	230

whereas other parameters (Table 3) for lauryl sulphate are higher than laurate at different temperatures.

Acknowledgement

The authors are thankful to College authorities for providing laboratory facilities and to the UGC, New Delhi for financial assistance.

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Iodine Clock Oscillating Reaction

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Manuscript received 29 May 1978, revised 26 December 1979, accepted 9 April 1980

Briggs and Rauscher[1] reported a new oscillating reaction, viz., oscillating iodine clock reaction. The reaction gives striking and excellent cyclic changes from colorless to gold to blue using simple reagents (potassium iodate, hydrogen peroxide, malonic acid, sulphuric or perchloric acid, manganese(II) or cerium(III) ion and starch) in proper concentrations. It resembles the iodate-hydrogen peroxide oscillating reaction of Bray-Liebhafsky[2,4,5] and also uses manganese or cerium which are components of Belousov-Zhabotinsky[3,4,6] reaction.

In this communication, the iodine clock oscillating reaction has been extensively studied using malonic acid and acetyl acetone in phosphoric acid medium. The concentration of each of the reactants has been systematically varied to determine the range of concentration where chemical oscillation is visible and to observe the resulting changes.

Three stock solutions are prepared separately and then mixed in equal volumes. One holds the hydrogen peroxide, another the iodate with phosphoric acid and the third, the malonic acid (or acetyl acetone), starch and manganese. This procedure has been changed when necessary and in all cases the concentrations in the table refer to concentrations in medium. The reaction mixture was continuously stirred at a more or less fixed rate with the help of a magnetic stirrer. The time period of oscillation was recorded visually.

Experimental

(Concentration ranges studied-See table)

Results and Discussion

In the sets (a) to (j) in the table, the following observations have been made.

(a) With 0.0055(*M*) malonic acid—a few oscillations which are not sharp. With 0.011(*M*) and 0.022(*M*) concns.—time period decreases with time. With 0.188(*M*) concn.—colorless to golden oscillation.

(b) With 0.073(*M*) H_2O_2—no visible oscillation. With 0.15(*M*) and higher concentrations—good oscillation.

(c) With 0.043(*M*) KIO_3—no viribie oscillation. With 0.046(*M*) and higher concns-good oscillation.

TABLE

	[Organic substrate*]	$[H_2O_2]$	$[KIO_3]$	$[H_3PO_4]$	$[Mn^{++}]$	[Starch]
a)	0.0055 (*M*) -0.188 (*M*)	1.2 (*M*)	0.0679 (*M*)	0.0426 (*M*)	0.0076 (*M*)	0.017%
b)	0.044 (*M*)	0.073 (*M*) -2.66 (*M*)	-do-	-do-	-do-	-do-
c)	-do-	1.2 (*M*)	0.043 (*M*) -0.061 (*M*)	-do-	-do-	-do-
d)	0.0451 (*M*)	-do-	0.065 (*M*)	0.0106 (*M*) -0.682 (*M*)	-do-	-do-
e)	-do-	-do-	-do-	0.0426 (*M*)	0.0019 (*M*) -0.071 (*M*)	-do-
f)	0.0014 (*M*) -0.089 (*M*)	1.2 (*M*)	0.063 (*M*)	0.0853 (*M*)	0.0066 (*M*)	0.0188%
g)	0.044 (*M*)	0.037 (*M*) -1.66 ()	0.0615 (*M*)	-do-	-do-	0.0177%
h)	-do-	1.2 (*M*)	0.031 (*M*) -0.062 (*M*)	-do-	0.071 (*M*)	0.023 %
i)	-do-	-do-	0.0662 (*M*)	0.064 (*M*) -0.6824 (*M*)	-do-	-do-
j)	-do-	-do-	0.063 (*M*)	0.0853 (*M*)	0.00166 (*M*) -0.22 (*M*)	0.0166%

*(a-e)-malonic acid
(f-j)-acetyl acetone

(d) With 0.0106(*M*) H_3PO_4—colorless to golden oscillations which are not sharp. With higher concentrations, faint blue-deep blue oscillation. With 0.682(*M*) concn.—variation of intensity of blue color with time not sharp.

(e) With 0.0019(*M*) Mn^{++}—color change not sharp. With 0.071(*M*) Mn^{++}—no observable oscillation. With intermediate concns.—good oscillation.

(f) With concentration of acetyl acetone in the range 0.0014(*M*)—0.022(*M*), only 2-3 oscillations observed. With 0.044(*M*), 0.0533(*M*) and 0.062(*M*) concns.—good oscillation. With 0.089(*M*) concn.-no visible oscillation.

(g) With 0.037(*M*) H_2O_2 as also with 1.66(*M*) H_2O_2—only 2 oscillations. With intermediate concns.—good oscillation.

(h) With 0.031(*M*) and 0.0408(*M*) KIO_3—no observable oscillation. With 0.044(*M*) and higher concentrations—good oscillation.

(i) With 0.064(*M*) H_3PO_4—no visible oscillation. With 0.6824(*M*) concn.—immediately blue precipitate. With intermediate concns.—good oscillation.

(j) With 0.00166(*M*)Mn^{++}—2 or 3 oscillations. With higher concns.—good oscillation.

The observations support the earlier observations in general that oscillations are possible only in a certain range of concentrations. In the present investigations induction periods are practically nil (less than 1 min) and in certain cases only a few oscillations are possible. Excellent color changes take place from colorless to golden to blue. The golden color however, is not always detectable. Reappearance of blue color (in case of malonic acid) or disappearance of blue color (in case of acetyl acetone) was noted in recording the periods of oscillation. In some cases, colorless to golden oscillation were recorded and in certain cases in later stages faint blue to deep blue oscillations were noted. In certain cases, the solutions become turbid and then oscillation starts. The time periods are of the order of a few seconds and the oscillations continue for several minutes. The oscillations are usually terminated by the appearance of a permanent blue color or precipitate. Time period gradually increases with time (decreases however in a few cases). In certain cases the increase in time period with time is remarkable.

Attempts have been made by different workers[6-10] for elucidating the mechanisms of oscillatory reactions. In as much as no oscillating reaction is well understood at present, little can be said of the mechanism of the iodine clock. If malonic acid is not present, manganese or cerium catalyses[1] a rapid initial formation of iodine. Malonic acid is a halogen consumer and halide producer in both B-Z reaction and the oscillating iodine clock.

The reaction may be considered[11,12] as switched rapidly between two steady states dependent on the iodide ion concentration and is thus composed of two gross phases.

A) The production of iodine via Mn(II) catalysed HIO_3-H_2O_2 reaction.

It would seem possible that a mechanism analogous to the $HBrO_3$ oxidation of Mn(II) in B-Z reaction is operative in the present case with consequent autocatalytic production of HIO_2 and subsequent rapid reduction of Mn(III) species by H_2O_2.

B) The consumption of iodine—iodide

The state responsible for production of iodine is dependent on the iodide concentration being low.

Thus as the iodide concentration rises there is reached a point when production of this state is inhibited and the iodine concentration no longer increases. Iodine, iodide and tri-iodide ions are now present and subject to at least four possible fates.

$$I_2+CH_2(COOH)_2 \rightarrow CHI(COOH)_2+I^-+H^+, \ I_2+CHI(COOH)_2 \rightarrow CI_2(COOH)_2+I^-+H^+ \quad ... (1)$$

$$I_2+5H_2O_2 \rightarrow 2IO_3^-+2H^++4H_2O \quad ... (2)$$

$$2I^-+H_2O_2+2H^+ \rightarrow I_2+2_2HO \quad ... (3)$$

$$5I^-+IO_3^-+6H^+ \rightarrow 3I_2+3H_2O \quad ... (4)$$

The principal consumption of iodine is via iodination of the organic species which is also the principal source of iodide ion. In the oscillatory system the iodination reaction together with the reoxidation of iodide produced maintains a steady state iodide concentration until the iodine concentration decreases appreciably. Eventually the iodide concentration decreases to a point where the production of the state responsible for production of iodine via the Mn II) catalysed reaction is no longer inhibited, the remaining iodide is rapidly removed and the cycle commenced again. Thus the reaction can be regarded as a series of autocatalytic reaction 'bursts' occurring with a certain frequeney.

We have to wait for sometime, however, for further elucidation of the mechanisms of these novel reactions.

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*p*H-Metric Studies of Schiff Base Complexes of Lanthanons

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Manuscript received 2 November 1979, accepted 20 December 1979

THE complexes of Pr(III), Nd(III), Gd(III) and Dy(III) with N-4-methylphenacylidene-*O*-aminophenol (MPAP) have been investigated by *p*H-metric titration technique as employed by Calvin and Melchior[1]. The protonation constant of the ligand and the stepwise formation constants of the metal chelates have been evaluated at constant ionic strength 0.25*M* $NaClO_4$ and temperature 30±1°.

Experimental

The ligand (MPAP) has been prepared and characterised by a similar method as reported earlier[2]. Lanthanon/chlorides or nitrates (B.D.H) were dissolved in double distilled water. The solutions were estimated gravimetrically by precipitating the metal oxalates and subsequent ignition and weighing as metal oxides. The solutions of required strength were then prepared by suitable dilution. Potassium hydroxide (B. D. H.) was washed by methanol two or three times in order to ensure the removal of carbonate. if any and then dissolved in methanol to obtain stock solution and its strength was determined by using standard oxalic acid solution.

Conditions of Study :

The *p*H-metric titrations were carried out at 30±1° with a Philips PP 9040 *p*H-meter as recommended by Zeidler[3] and Fritz[4].

The instrument was standardised against 0.05*M* solution of potassiumhydrogenphthalate. The volume of the solutions to be titrated was always kept constant (20 ml) by mixing with necessary volume of methanol. The following three mixtures (a), (b) & (c) were prepared for each system and titrated against standard alkali.

(a) 10.0 ml of ligand (0.025*M*)+5.0 ml of 1*M* $NaClO_4$

(b) 10 ml of ligand (0.025*M*)+5.0 ml of 1*M* $NaClO_4$+1.0 ml of metal salt solution (0.005 *M*).

(c) 10.0 ml of ligand (0.025 *M*)+5.0 ml of 1*M* $NaClO_4$+2.0 ml of metal salt solution (0.005 *M*).

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TABLE 1—pK VALUE OF LIGAND (MPAP) IN METHANOL

Vol. of KOH (0.1M) in ml.	0.0	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.25
pH	5.20	5.85	6.50	6.75	6.85	7.00	7.20	7.30	7.35	7.40
nH	1.00	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10

pK value from Fig. No. 1 $=1.0\times10^{-7.0}$.

Results and Discussions

The protonation constant is determined by plotting pH values of the solution resulting from progressive addition of standard alkali to ligand solution of known strength vs nH values (where nH=average number of protons associated with a ligand).

$$nH=\frac{\text{Total number of } H^{+} \text{bound to R}}{\text{Total number of ligand mole present}}$$

$$\therefore \quad nH=\frac{[RH]}{[R^{-}][H^{+}]}=\frac{R^{-}-P-H^{+}+GH^{-}}{R^{-}}$$

where R^{-}=Total concentration of the ligand, P=The concentration of alkali added.

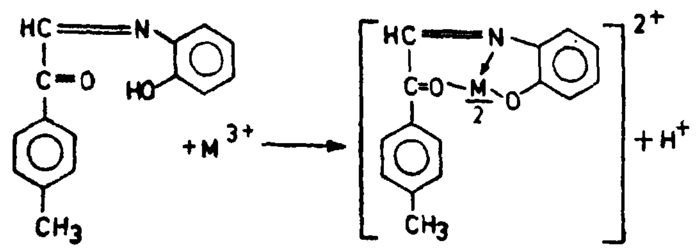
The correct value of pK is obtained from Fig. No.1 as pH where nH=0.5 present in the system. Titrations of the ligand with and without metal ion are performed against KOH. The curves are drawn between pH vs volume of alkali added. The horizontal distance between the two curves at any value of pH gives the amount of proton liberated by chelation i.e., the amount of ligand complexed. This value divided by the total amount of metal ion in the system gave $\bar{n}$. Thus at various values of pH a set of $\bar{n}$ values is determined. The values of $\bar{n}$ were plotted against the corresponding values of-log L. The final values of log K_1 and log K_2 as shown in Table 2 are equal to the values of-log L at $\bar{n}$=0.5 and 1.5 respectively.

The calculations were made by taking 1.0×10^{-7} as dissociation constant of the ligand. The gradual increase in the value of $\bar{n}$ with the increase of pH

TABLE 2—METAL-LIGAND APPARENT STABILITY CONSTANTS OF THE CHELATES, μ=0.25M($NaClO_4$), TEMP. 30+1°C

System	Fig. No.	Curve No.	log K_1	log K_2	log β
$Pr^{3}\pm$MPAP	2	I	2.875	0.55	3.425
		II	2.25	0.05	2.30
$Nd^{3}\pm$MPAP	3	I	2.80	0.60	3 40
		II	2.15	0.05	2.20
$Gd^{3}\pm$MPAP	4	I	2.65	0.50	3.15
		II	2.10	0.05	2.15
$Dy^{3}\pm$MPAP	5	I	2.10	0.60	2.70
		II	1.95	0.05	2.00

In order to determine the stepwise formation constants of a chelate, Bjerrum[6], introduced the concept of degree of formation defined as the average number of ligands ($\bar{n}$) bound per metal ion showed that the anionic form of the ligand was responsible for the complex ion formation with Pr(III), Nd(III), Gd(III) and Dy(III). The complexation reaction is as follows :



PROTON-LIGAND FORMATION CURVE

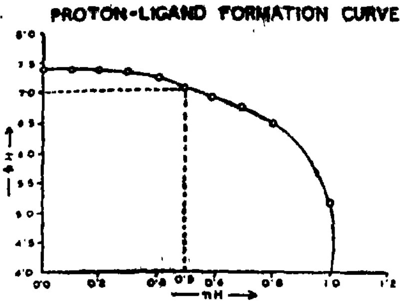


FIG. 1 0

METAL-LIGAND FORMATION CURVES

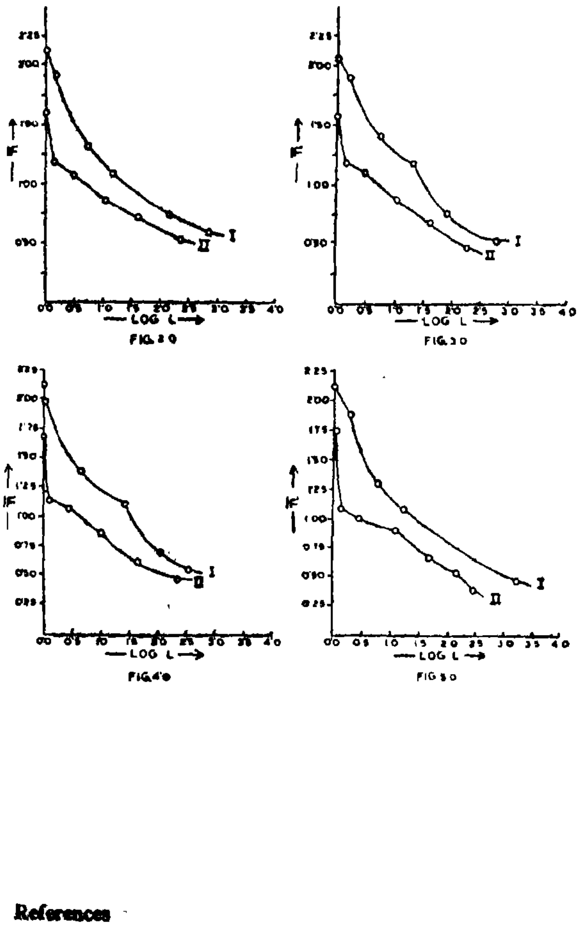


FIG. 2 0 FIG. 3 0 FIG. 4 0 FIG. 5 0

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Studies on Stable Ylids : Synthesis of 9-Arylidene 2, 7-Dibromofluorenes Via 2, 7-Dibromofluorenylidenetriphenylphosphorane

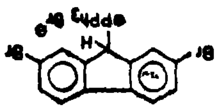
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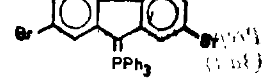
Manuscript received 16 March 1979, revised 12 September 1979, accepted 9 April 1980

THE reactions of fluorenylidenetriphenylphosphorane have been extensively studied with substituted benzaldehydes yielding benzalfluorenes as Wittig products[1-3]. But the effect of substituents which could enhance the reactivity of such ylid has not been examined. Although the stabilized ylid, 2, 7-dibromofluorenylidenetriphenylphosphorane, was synthesized in 1962 by Schoenberg *et al*,[3] yet its synthetic utility has not been investigated so far. Continuing our researches into the reactivity and synthetic utility of the ylids[4-11], we now wish to report the effect of bromine atom on the reactivity of 2, 7-dibromofluorenylidenetriphenylphosphorane with substituted aromatic aldehydes.

Treatment of the salt-2, 7-dibromofluorenyltriphenylphosphonium bromide (1), prepared by the quaternization of triphenylphosphine with 2, 7, 9-tribromobenzalfluorene, with 30% NH_4OH in boiling enthanol gave ylid-2, 9-dibromofluorenylidentriphenylphosphorane (2) which on subsequent reaction with a series of aromatic aldehydes afforded 9-arylidene-2, 7-dibromofluorenes(3a-j) in 50-90% yields. Ylid (2), however, failed to undergo reaction with aromatic ketones even after prolonged refluxing. The Ylide (2) was found to be more nucleophilic than fluorenylidenetriphenylphosphorane[1] since former coupled quickly with the aldehydes and yielded products (3a-j) in better yields. One of the most plausible reasons to the enhanced nucleophilicity is the +M effect exerted by the bromine atoms on the fluorene nucleus.



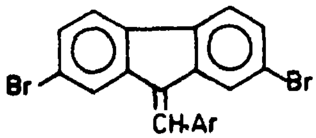
1



2

The fluorene derivatives (3a–j) gave satisfactory elemental analyses and melting points for known compoundsand/were in accordance with that reported in literature[11-13]. The IR spectra of 3a–j showed absorption bands at 1600-1585 cm^{-1} (νC=C) and 970-940 cm^{-1}. The latter absorptions are associated

Table 1—Physical Properties of 9-arylidene-2, 7-dibromofluorenes (3a-j)



Compound	Ar	Yield %	M.P. °C	Crystn. solvent	Molecular formula	Analysis found (Calcd.) % C	H
3a	C_6H_5	60	96-98a	AcOH	$C_{20}H_{12}Br_2$	58.28 (58.25)	2.93 (2.91)
b	$3\text{-}NO_2C_6H_4$	75	155-56b	$CHCl_3$	$C_{20}H_{11}NO_2Br_2$	52.48 (52.51)	2.43 (2.41)
c	$4\text{-}NO_2C_6H_4$	90	195-97c	AcOH	$C_{20}H_{11}NO_2Br_2$	52.55 (52 51)	2.40 (2.41)
d	$4\text{-}ClC_6H_4$	65	213-15d	AcOH	$C_{20}H_{11}Br_2Cl$	53.71 (53.75)	2.45 (2.46)
e	$4\text{-}CH_3C_6H_4$	55	136-38e	$CHCl_3$	$C_{21}H_{14}Br_2$	59.19 (59.15)	3.26 (3.28)
f	$4\text{-}CH_3OC_6H_4$	56	134-35f	AcOH	$C_{21}H_{14}Br_2O$	57.04 (57.01)	3 14 (3.17)
g	6-Br-3, 4-di-$(CH_3O)C_6H_2$	50	202-03g	AcOH	$C_{22}H_{15}Br_3O_2$	47.98 (47.91)	2.79 (2.72)
h	3, $4\text{-}O_2CH_2C_6H_3$	55	118-20h	$CHCl_3$	$C_{21}H_{12}Br_2O_2$	55.29 (55.26)	2.66 (2.63)
i	$2\text{-}C_4H_3O$	58	192-94i	AcOH	$C_{18}H_{10}Br_2O$	53.70 (53.73)	2.43 (2.48)
	$\text{-}CH{=}CH\text{-}C_6H_5$	55	204-5j	AcOH	$C_{22}H_{14}Br_2$	60.21 (60.27)	3.22 (3.20)

a. Lit.[12] 98-99 ; b. Lit.[12] 154-55 ; c. Lit.[12] 195-96 ; d. Lit.[12] 211-12 ; e. Lit[12] 140 ; f. Lit.[12] 132-33 ; g. and h. unreported , i. Lit.[12] 190-91 , j. Lit.[12] 206-07.

with out of plane deformations of hydrogen attached to exocyclic double bond[13]. The NMR spectra of 3a – j in general exhibited olefinic protons in the range of δ 6.60-7.35 and aromatic protons at δ 6.65-8.65.

Experimental

The ylid (2) and its precusor (1) weresynthesized following the procedure cited in the literature[8]. Melting points determined on a Gallenkamp apparatus are uncorrected. The IR spectra (KBr) were recorded on a Perkin-Elmer spectrophotometer. The NMR spectra were run on Varian A-60 spectrophotometer. All the products were separated and purified by column chromatography over neutral alumina. Purity was checked by TLC.

Preparation of 9-arylidene-2, 7-dibromofluorenes (3a-j):

To a solution of 4 m mole of ylid (2) in 100 ml of chloroform, was added in an atmosphere of nitrogen, 4 m mole of aromatic aldehydes. The mixture was refluxed on a steam bath for 4-8 hrs and solvent was removed under pressure on a steam bath. The resulting solid was chromatographed over neutral alumina. The elution with benzene-pet. ether (4 : 1) gave 9-arylidene-2, 7-dibromofluorenes (3a - j) in 50-90% yields which were crystalized from appropriate solvents given in Table 1.

Acknowledgement

The authors thank Dr. S. D. Shukla, H.B.T.I., Kanpur-2, India, for providing facilities. One of the authors SCC thanks C.S.I.R., New Delhi (India) for the award of Senior Research Fellowship. KCG thanks U.G.C., New Delhi, for the award of a Teacher Fellowship.

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Studies on the Synthesis of Heterocyclic Compounds-Part-II. Synthesis of 1-hydroxy-and 1-aryl-3-substituted-4-keto-3, 4-dihydrophthalazines, 1-hydroxy-4-aryl- and 1, 4-dihydroxy-phthalazines

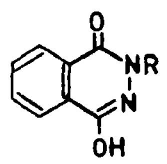
A. C. DESAI and C. M. DESAI

P. T. Sarvajanik College of Science, Surat

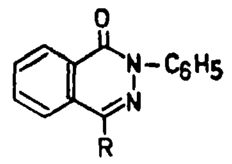
Manuscript received 7 February 1979, revised 20 November 1979, accepted 4 March 1980

IN the previous communication,[1] the use of polyphosphoric acid (PPA) was reported as a condensing agent in the synthesis of 1-hydroxy-3-substituted-4-keto-3, 4-dihydrophthalazines(I). It has been observed that this agent is very effective in giving these phthalazines in very high yields of clean products in a comparatively shorter time.

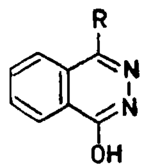
Chattaway and Tesh[2], observed that when N-arylamino-phthalimide was refluxed with alcoholic sodium ethoxide in sealed tube for 12 hours, it was rearranged into (I) ; 1-hydroxy-3-aryl-3, 4-dihydrophthalazine-4-acetic acids were oxidised by aqueous permanganate[3-6] to (I) at 70-100° ; Rowe, Peters and Rangwala[7] obtained (I) by demethylation of *o*-methyl ether of (I) with hydrobromic acid ; Rowe, Le'cutier and Peters[8] obtained amino derivatives of (I) by reduction of corresponding nitro compounds with stannous chloride and hydrochloric acid. Roser[9],



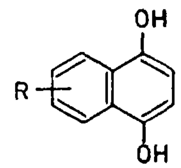
(I)



(II)



(III)



(IV)

obtained 1-aryl-3-phenyl-4-keto-3, 4-dihydrophthalazine(II) by refluxing the *o*-keto acid and the arylhydrazine in alcohol. Bromberg[10] and Rothenberg[11], obtained 1-hydroxy -4-benzylphthalazine(III) and 1-hydroxy-4-phenylphthalazine(III), respectively from benzalphthalide and *o*-benzoylbenzoic acid in hot alcohol with hydrazine hydrate. For the synthesis of 1, 4-dihydroxy phthalazines(IV), various refluxing agents have been used. Drew and Hatt[12], refluxed the reactants for 4 hours with sodium acetate and acetic acid (IV, R=H) ; Drew and Pearman,[13] refluxed 3-nitrophthalimide and aqueous hydrazine hydrate for 6 hours (IV, R=5-NO_2) and also for 16 hours an ammoniacal mixture of 6,7-dichloro-1, 4-dihydroxy phthalazine and cuprous iodide for obtaining 6, 7-diamino-1, 4-dihydroxyphthalazine ; while 5-methylamino-1, 4-dihydroxyphthalazine and 5, 8-diamino-1, 4-dihydroxyphthalazine were obtained by heating respective phthalimide and hydrazine hydrate (3*M*) for one hour ; Marriott and Robinson[14] refluxed N-arylphthalimide and hydrazine hydrate in boiling pyridine ; Huntress, Stainly and Parker[15], heated 1,2,3-$NO_2(COOH).C_6H_3.CONHNH_2$, at 160° for 12 hours.

Experimental

1-Hydroxy-3-substituted-4-keto-3,4-dihydrophthalazines (I) :

A mixture of phthalic anhydride (0.03*M*) and mono N-substituted hydrazine (0.03*M*) was heated on a sand bath with PPA (H_3PO_4 : P_2O_5 : : 12 ml : 20 g) at 160° for 30 minutes and allowed to cool. The mass was decomposed with ice water and crystallised from acetic acid. Phthalazines(I) newly prepared are : 3-amido, m.p. 320° ; yield 96% (Found : N, 20.6%. Calcd. for $C_9H_7O_3N_3$ N, 20.5%) ; 3-thioamido, m. p. 307° ; yield 92% (Found : N, 19.2%, Calcd. for $C_9H_7O_2N_3S$ N, 19.00%).

1-Aryl-3-phenyl-4-keto-3, 4-dihydrophthalazines(II) :

A mixture of *p*-substituted-*o*-aroylbenzoic acid (0.02*M*) and phenylhydrazine (0.02*M*) was heated at 100° for 3 minutes and the resulting hydrazone[16] was treated with PPA at 160° for 30 minutes. The cold syrupy mass was decomposed with ice water and crystallised from absolute alcohol. 1-Arylphthalazines(II) newly prepared are : *p*-methylphenyl, m. p. 139° ; yield 66% (Found : N, 9.05%. Calcd. for $C_{21}H_{16}N_2O$ N, 9.0%) ; *p*-chlorophenyl, m. p. 165° ; yield 70% (Found : N, 8.50%. Calcd. for $C_{20}H_{13}N_2OCl$ N, 8.40%) ; *p*-bromophenyl, m.p. 143° ; yield 68% (Found : N, 7.65%. Calcd. for $C_{20}H_{13}N_2OBr$ N, 7.43%).

These phthalazines(II) are colourless microcrystalline solids, insoluble in dilute acid and alkali and soluble in common organic solvents.

1-Hydroxy-4-aryl-phthalazines (III) :

A mixture of *p*-substituted-*o*-aroylbenzoic acid (0.02*M*) and hydrazine sulphate (0.02*M*) was heated on a sand bath with PPA at 160° for 30 minutes and the mass was decomposed with ice water and crystallised from acetic acid. Phthalazines (III) prepared are : *p*-methylphenyl, m.p. 248° ; yield 88% (Found : N, 11.85%. Calcd. for $C_{15}H_{12}N_2O$ N, 11.90%) ; *p*-chlorophenyl, m.p. 266° ; yield 84% (Found : N, 11.0%. Calcd. for $C_{14}H_9N_2OCl$ N, 10.9%) ; *p*-bromophenyl, m. p. 266° ; yield 86% (Found : N, 9.25%. Calcd. for $C_{14}H_9N_2OBr$ N, 9.3%).

Phthalazines(III) are colourless crystalline solids, sparingly soluble in organic solvents, soluble in dilute alkali, insoluble in dilute mineral acids and are characterised by high melting points. They give cherry red colouration with alcoholic ferric chloride.

1,4-Dihydroxyphthalazines (IV) :

A mixture of phthalimide (0.03*M*) and 99% hydrazine hydrate (0.032*M*) was heated on a sand bath with PPA at 220° for 30 minutes and allowed to cool. The mass was decomposed with ice water and crystallised from acetic acid-ethanol (1 : 2) mixture. 6-Benzoylamino-1, 4-dihydroxyphthalazine is newly prepared (m. p. 329°d ; yield 86%).

1, 4-Dihydroxyphthalazines are characterised by high melting points with decomposition, they give reddish-brown colouration with alcoholic ferric chloride.

Further work along this line is in progress.

Acknowledgement

One of us (ACD) is grateful to the college authorities for providing research facilities.

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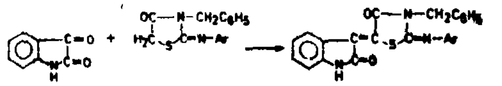
Synthesis of New 5-(2-Oxo-3-Indolinylidene)-3-Benzyl-2-Arylimino-4-Thiazolidinones Derived from 3-Benzyl-2-Arylimino-4-Thiazolidinones

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Manuscript received 4 April 1979, accepted 4 March 1980

CONDENSATIONS of 3-aryl-2-arylimino-4-thiazolidinones with isatin has been reported to yield thioindigoid dyes[1,2]. Using this approach, new



(1) (2) (3)

seventeen 5-(2-oxo-3-indolinylidene)-3-benzyl-2-arylimino-4-thiazolidinones (3) (Table 1) have been prepared by condensing isatin (1) with 3-benzyl-2-arylimino-4-thiazolidinones (2) in the presence of anhydrous sodium acetate and glacial acetic acid. Various 3-benzyl-2-arylimino-4-thiazolidinones were obtained from 1-benzyl-3-aryl-2-thioureas and monochloroacetic acid[3]. These dyes were coloured from deep-orange to dark-red and dissolved in concentrated sulphuric acid producing dark co loured solution.

TABLE 1—5-(2-OXO-3-INDOLINYLIDENE)-3-BENZYL-2-ARYLIMINO 4-THIAZOLIDINONES (3)

S. No.	Ar.	Yield	m.p. °C	Colour
1.	*o*-Tolyl	77	190	dark-red
2.	*p*-Tolyl	77	205	dark-red
3.	*o*-Phenetyl	86	212	orange-red
4.	*p*-Phenetyl	79	205	orange-red
5.	*p*-Fluorophenyl	70	200	dark-red
6.	*o*-Chlorophenyl	71	116	dark-red
7.	*p*-Chlorophenyl	80	95	dark-red
8.	*o*-Bromophenyl	81	150	dark-red
9.	*p* Bromophenyl	81	125	dark-red
10.	*p*-Iodophenyl	91	180 (decompn.)	Red
11.	2,5-Dichlorophenyl	73	135 (decompn.)	dark-red
12.	*o*-Hydroxyphenyl	77	70 (melts with charring)	blackish-red
13.	*m*-Hydroxyphenyl	84	75 (decompn.)	red
14.	*p*-Hydroxyphenyl	77	170 (decompn.)	blackish-red
15.	4-Hydroxy-2-methylphenyl	71	175	dark-red
16.	1-Naphthyl	72	volatile at 260°	red
17.	2-Pyridyl	76	280	bright-red

Experimental

All melting points have been taken in open capillary tubes and are uncorrected.

The following general procedure as exemplified for the synthesis of 5-(2-oxo-3-indolinylidene)-3-benzyl-2-(1-naphthylimino)-4-thiazolidinone was adopted for the preparation of all the thioindigoid dyes.

A mixture of 3-benzyl-2-(1-naphthylimino)-4-thiazolidinone (3.32g, 0.01 mole), isatin (1.5g, 0.01 mole), anhydrous sodium acetate (3.2g, 0 04 mole), glacial acetic acid (40 ml) and acetic anhydride (4ml) were refluxed for about 4.5 hrs. After cooling the reaction mixture was poured into cold water when a red precipitate was formed. The precipitate was filtered, washed successively with hot water, dilute acetic acid and finally several times with ethanol and dried.

The IR spectrum (nujol) showed characteristic peaks at 3200 cm^{-1} (NH) ; 2950, 2880 cm^{-1} (CH_2) ; 1740, 1720 cm^{-1} (C = O) ; 1650 cm^{-1} (aliphatic C = C) ; 1615 cm^{-1} (C = N) ; 1596, 1480 cm^{-1} (aromatic C = C) and 740 cm^{-1} (C — S).

All of them showed consistent elemental analysis.

Acknowledgement

The author is grateful to (late) Dr. R. P. Rao, Reader in Chemistry, University of Gorakhpur, Gorakhpur for his keen interest in the work.

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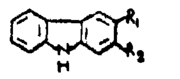
A New Synthesis of Murrayacinine

S. ROY and D. P. CHAKRABORTY

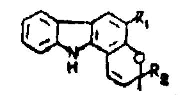
Bose Institute, Calcutta-700 009

Manuscript received 4 April 1979, revised 20 December 1979, accepted 9 February 1980

In a previous communication, we reported the structure and synthesis of murrayacinine (I), a carbazole alkaloid isolated from the stem-bark of *Murraya koenigii* Spreng. The synthesis involved condensation of citral with 2-hydroxy-3-formyl carbazole (II) which in turn was obtained by chromic acid oxidation of 2-hydroxy-3-methyl carbazole (III). In consideration of the relatively poor yield of the alkaloid obtained in our previous synthesis and in view of the fact that murrayacinine (I) is an oxidative variant of the alkaloid mahanimbine (IV)[2], a facile conversion of IV to I was achieved by the use of DDQ (dichloro-dicyano benzoquinone), a reagent that has recently been used[3-5] for similar oxidation of aromatic methyl groups to corresponding formyl groups. Mahanimbine in dry benzene was stirred with DDQ at room temperature for 2 hours. The product was then taken in ether, washed with 1% NaOH and water. From the reaction mixture murrayacinine was isolated by preparative thin layer method.



II, III



I, IV

(I) R_1 = -CHO ; R_2 = $CH_2.CH_2.CH{=}C(CH_3)_2$

(II) R_1 = -CHO ; R_2 = —OH

(III) R_1 = $-CH_3$; R_2 = —OH

(IV) R_1 = $-CH_3$; R_2 = $CH_2.CH_2.CH{=}C(CH_3)_2$

Experimental

Mahanimbine (50 mg) in dry benzene (10 ml) was stirred and a solution of DDQ in dry benzene (molar proportion) was added to it over a period of 15 minutes. The stirring was continued for 1 hour at room temperature. The reaction product was then treated with 1% NaOH and extracted with ether. The ether solution was washed with water to free it from alkali and dried over sodium sulphate.

After the removal of the ether the residue was taken in benzene and subjected to preparative t. l. c. The spot identical with natural murrayacinine was scraped out from the t.l.c. plate, extracted with alcohol and filtered. The solid obtained on evaporation of the alcohol was purified and recrystallised from benzene-petroleum ether mixture. The compound was finally identified as murrayacinine (yield 15 mg) by a direct comparison with a pure specimen of the sample (uv, ir, m.p., m.m.p., t.l.c.). The other constituents in the chromatogram was not characterised due to poor yield.

Acknowledgement

The authors wish to thank Dr. A. Sen, Head of the Dept. of Chemistry and Dr. S. C. Bhattacharyya, Director for their interest in the work.

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Triterpenoids of Indian Dilleniaceae

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Manuscript received 25 May 1979, revised 2 February 1980, accepted 9 April 1980

In consideration of previous work[1-4] and our taxonomic interest in the family Dilleniaceae we have examined the leaves of all the twelve indigenous species of Dilleniaceae[5] with the aim of isolating and identifying the triterpenes and sterols. Table 1 summarizes our findings, which show that besides the widely distributed β-sitosterol, triterpenes of the lupene series *viz.*, lupeol, betulin and butulinic acid occur in all the twelve species examined.

TABLE 1—COMPOUNDS ISOLATED FROM DILLENIACEAE SPECIES (PERCENTAGE YIELD/DRY WT).

Name of the species	betulinic acid	betulin	lupeol	β-sitosterol
Acrotrema arnothianum Wight	0.53	0.065	0.03	0.019
Dillenia andamanica Parkinson	0.50	0.082	0.02	0.015
D. aurea Smith	0.72	0.045	0.09	0.025
D. bracteata Wight	0.58	0.070	0.08	0.016
D. indica Linn	0.60	0.105	0.015	0.012
D. pentagyna Roxb.	0.98	0.150	0.01	0.010
D. retusa Thunb.	0.85	0.068	0.008	0.006
D. scabralla (D. Don) Roxb. exWall	0.575	0.120	0.032	0.022
Tetracera akara (Burm.f.) Merr.	1.05	0.045	0.045	0.005
T. indica (Houtt. ex Christm. & Panz., Merr.)	0.60	0.01	0.014	0.030
T. sarmentosa (L.) Vahl. subsp. andamanica (Hoogl.) Hoogl.	1.23	0.070	0.006	0.004
T. scandens (L.) Merr.	1.35	0.030	0.005	0.001

Experimental

Air dried and milled leaves were extracted with hot rectified spirit for 30 hrs. The semisolid mass obtained on evaporation of solvent was triturated exhaustively with ether. Ether insoluble residue being negligible was discarded. From ether soluble portion the triterpenes and sterol were isolated by chromatography over silica-gel and preparative tlc. The triterpenoids and sterol were identified by direct comparison with authentic samples[6] (tlc, mmp, ir) and preparation of derivatives.

Betulinic acid crystallised from methanol, m.p. 306-309°, $[\alpha]_D+6°$ (Ethanol). On treatment with diazomethane methyl betulinate was obtained, crystallised from methanol, m.p. 222-224°. The methyl ester yielded acetate with pyridine-Ac_2O. It was crystallised from ethanol, m.p. 198-201°, $[\alpha]_D$ $+20°$ ($CHCl_3$). Betulin crystallised from benzene-methanol m.p. 252-254°, $[\alpha]_D+19°$ ($CHCl_3$). Acetate prepared, as above, crystallised from methanol, m.p. 220-224°, $[\alpha]_D+21°$ ($CHCl_3$). Lupeol crystallised from ethanol, m p. 210-212°, $[\alpha]_D+22°$ ($CHCl_3$). Acetate crystallised from ethanol m.p. 209-212°, $[\alpha]_D+43°$ ($CHCl_3$). β-sitosterol crystallised from methanol, m.p. 136-137°, $[\alpha]_D-35°$ ($CHCl_3$), acetate, m.p. 126-127°, $[\alpha]_D-35°$ ($CHCl_3$).

Acknowledgement

The authors thank Dr. S. K. Jain, Director, Botanical Survey of India, Howrah-3 for providing facilities. We record our thanks to Dr. S. C. Pakrashi, Deputy Director, Indian Institute of Experimental Medicine, Calcutta-32 for rotation and IR spectra.

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Chemical Examination of Essential Oil of *Lantana orangemene*

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Manuscript received 17 August 1979, revised 17 March 1980, accepted 9 April 1980

The genus Lantana (Fam-Verbenaceae) has about 50 species mostly American, grown in tropical and sub-tropical regions[1]. Only few species of Lantana are found to grow in Rohilkhand region of U. P. *Lantana orangemene* (flower orange) appears to be very much related to *Lantana camara*, botanically.

But the presence of *Lantana camara* proper in India is doubtful[2]. The decoction of leaves is given in tetanus, malaria and rheumatism by the local people. Though few scientists have reported the chemistry of essential oil of *Lantana camara*[3,4] and its varieties[5], no work is available in literature on *Lantana orangemene*.

The essential oil from the leaves has been extracted by steam distillation in 0.2% yield. The pale yellow volatile oil was found to possess the following physico-chemical constants :

Specfic) gravity (0.88407), optical rotation (+2.212, ref. index (1.5492), acid value (1.874), ester value (26 98), carbonyl value (11.09%) and acetylaton value (99.48).

Different constituents of the oil were separated by kissel gel columins (1 0×4.5 cm) using the solvent benzene-ethylacetate (95 : 5). The separated fractions were tested for their purity on TLC(Plates-0.25 mm thick) and the isolated terpenes were identified by their ref. index, optical rotation, IR, NMR and co-TLC. IR measurements were made on Perkin-Elmer-457 infracord and NMR on Varian A-60D.

The isolated terpenes(%) are d-limonene(2.24), α-pinene (1.28), β-pinene(2.12), α-terpinene(1.80), β-caryophyllene(2.60), citral (4.04), 1,8-cineole(5.38), linalool (11.24), geraniol (18.64), α-terpeniol (3 44), menthol (8.24), dipentene (3.40) and β-phellandrene (21.92).

The presence of these constituents was also confirmed by GLC. The GLC was carried out in a gas chromatograph model-900B and other conditions were as follows :

Column-UCCW 982 10% 1.8 m

Temp. of column-100° 16 min
300° 4°/min.
250°

carrier gas-Nitrogen (30 ml/min)
Chart speed-5 mm/min.

Amount introduced-5 μl

Detector-FID

The presence of β-phellandrene, d-limonene, β-pinene, α-terpinene and menthol are reported for the first time in the oil of Lantanagenus. Difference in the chemical composition and physico-chemical constants of the oil obtained from the leaves of *Lantana orangemene* than that of *Lantana camara*[8] clearly shows that both the plants are different.

Acknowledgement

Thanks are due to Dr. O. Seligmann and Dr. G. Tittle of Institut für Pharmazeutische Ärzneimittellehre, München (W. Germany) for IR, NMR measurements and GLC. Thanks are also due to U.G.C. for financing research project sanctioned to one of us (RKB) under which this work could be done.

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Chemical Investigations of *Anagallis arvensis* Flowers

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Manuscript received 21 July 1979, accepted 4 March 1980

In furtherance of studies[1,2], the flowers of *Anagallis arvensis* have been found to contain three phytosterols (stigmasterol, β-sitosterol, α-spinasterol 3-glucoside) and three flavonoids (kaempferol, quercitin and rutin).

Experimental

Air dried flowers (275 g) of herb were soxhleted with 95% ethanol. The greenish sticky residue (20%) after defatting with n-hexane, was triturated with petroleum ether 60-80° (Fraction I ; 15 mg).

The brown defatted residue on washing with absolute methanol left behind undissolved shining flakes (Fraction II ; 100 mg).

The solid mass, obtained on removal of methanol under vacuum, was triturated with ether (Fraction III ; 50 mg) leaving undissolved residue (Fraction IV).

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Fraction I : It responded to positive Libermann-Burchard and Salkowski reactions indicating the presence of steroidal nucleus. Co-TLC with authentic samples employing n-hexane : ethyl acetate (5 : 1)[5] and benzene : ethyl acetate (4 : 1)[4] ascertained the presence of stigmasterol and β-sitosterol in this fraction.

Fraction II : It gave positive Molisch's test besides usual tests for sterol. It was crystallised from chloroform : methanol to colourless flakes (m.p. 290° ; lit m.p. 292°)[5]. Elemental analysis showed C, 73.56% ; H, 9.88% (required C, 73.17% ; H, 10.10% for $C_{35}H_{58}O_6$).

It was characterised as α-spinasterol 3-glucoside by infrared studies.

Co-TLC, Co-IR studies and the preparation of derivatives of aglycone further supported the identification.

Fraction III : It was found to have two flavonoidal aglycones by paper and thin layer chromatography. Separation by borax-complex formation method yielded kaempferol 12 mg (m.p. 276-8° ; lit. m.p. 279°)[6] ; λ^{MeOH}_{Max} 267, 366 (sh), 367 nm and quercetin 15 mg (m.p. 310° ; lit. m.p. 316°)[6] ; λ^{MeOH}_{Max} 256, 269 (sh), 300 (sh), 368 nm.

The identities were further confirmed by Co-chromatography, Co-UV studies with the authentic samples and derivative preparation.

Flavonoidal substance from *fraction IV* was isolated by precipitation with basic lead acetate and was characterised as rutin 60 mg (m.p. 190-1° ; lit. m.p. 188-190°) ; λ^{MeOH}_{Max} 257, 268 (sh), 295 (sh); 360 nm.

Undepressed mixed melting point, Co-chromatography and Co-UV studies further supported the identification.

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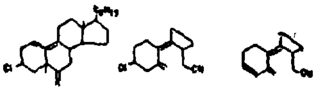
Second Order Beckmann Rearrangement of 3β-chloro-19-nor-5-methyl-5β-cholest-9 (10)-en-6-one Oxime

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Manuscript received 7 February 1979, accepted 4 March 1980

IN continuation of reports on azasteroids[1,2], we subjected compound(II) to Beckmann rearrangement which provided single nitrile (III). The product (III) on base hydrolysis resulted into dehydrohalogenated compound(IV). The structures of (III) and (IV) have been established on the basis of elemental and spectral evidences.



(I) X = O (II) X = N-OH (III) (IV)

The ketone (I), (m.p. 63-64°) was prepared according to the procedure described by Aebli *et al.*[3] and was converted by the general oximation method[4] to its oxime (II), crystallized from ethanol m.p. 135° (positive Beilstein test), (Found : C, 74.79 ; H, 10.21 ; N, 3.35. $C_{27}H_{44}ONCl$ requires C, 74.82 H, 10.16 ; N, 3.23%). IR spectrum gave peaks at 3220 (OH), 1670 (C=N−OH) and 745 cm^{-1} (C-Cl). The n.m.r. spectrum of (II) exhibited signals at 9.2br,s (O*H*, disappeared on addition of D_2O), 4.4m (C3-α*H*, $W\frac{1}{2}$=9 Hz), 1.5s (C5-CH_3), 0.9 and 0.8 (other methyls).

The oxime (II) (500 mg) on treatment with thionyl chloride (10 ml) at-20° followed by treatment with an excess of 4*N* KOH (25 ml) afforded a sticky coloured material, which on passing through neutral alumina gave 3β-chloro-5, 6-secocholesta-19-nor-9(10), 5(19)-dien-6-onitrile (III) as a noncrystallizable oil (150 mg). The homogeneity of the oily product(III) was checked by TLC. The nitrile(III) gave positive Beilstein test, (Found : C, 77.89 ; H, 10.12 ; N, 3.50. $C_{27}H_{42}ClN$ requires C, 78.07 ; H, 10.12 ; N, 3.37%). The i.r. spectrum showed bands at 2240 (C≡N), 1630 (C=C) and 750 cm^{-1} (C−Cl). The n.m.r. spectrum gave a broadened singlet at δ 5.42 which is easily ascribable for =C19-H_2(vinylic methylene protons). A broad multiplet for C3-proton was observed at δ 4.25 (C3-α*H*, $W\frac{1}{2}$=16 Hz). Other signals were seen at δ 0.91, 0.81 and 0.68 (other methyls). The u.v. spectrum of (III) gave absorption maxima at 215 nm which proves the presence of diene system.

The oxime (II) (500 mg) was treated with *p*-toluenesulphonyl chloride (500 mg) and pyridine (4 ml) in the usual manner. After work up, and passing through neutral alumina gave (III) (TLC, IR and

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NMR identical with the sample obtained using $SOCl_2$).

The nitrile (III) (100 mg) on hydrolysis with 2% methanolic KOH (10 ml) and usual work up procedure gave 5,6-secocholesta-19-nor-3(4), 5(19), 9(10)-trien-6-onitrile (IV) as an oil (60 mg), (Found : C-84.98 ; H, 10.91 ; N, 3.52. $C_{27}H_{41}N$ requires C, 85.48 ; H, 10.81 ; N, 3.69%). In i.r. spectrum bands were observed at 2240 (C≡N) and 1635cm^{-1}

C
‖
(-C=C−C−C=C-). The n.m.r. spectrum showed a broad unresolved multiplet centred at δ 5.63 ascribable for 4-vinylic protons (C3-1H, C4-1H,=C19-H_2), δ 0.71 (C13·CH_3), 0.93 and 0.83 (other methyls). U. V. shows the absorption maxima at 270 nm which also confirmed the extension of conjugation of diene.

Acknowledgement

We are thankful to CSIR, New Delhi for financial help, Head, Department of Chemistry for providing necessary facilities and Prof. M.S. Ahmad for useful discussion.

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J. Indian Chem. Soc.,
Vol. LVII, July 1980, pp. 764

BOOK REVIEW

Diosgenin and Other Steroid Drug Precursors by L. V. ASOLKAR & Y. R. CHADHA, Publication and Information Directorate, CSIR, Hillside Road, New Delhi-110 012, 1979, pp XII +170, Price Rs. 32/-.

The book is intended to serve as a compendium on the various facets of steroid industry with special reference to India. As Indian steroid industry is mainly based on diosgenin it is not surprising that the book deals diosgenin in greater details than the other steroid drug precursors. The book provides necessary background to research workers engaged in R & D work on steroid drugs and their intermediates.

The book is divided into six chapters. Chapter 1 deals with chemical background, history of steroid development, discovery of diosgenin and cortisone, trends of other steroid drugs precursors and present position of steroid industry in India.

Chapter 2 describes some species of Dioscorea which are chief sources of diosgenin in India including economics of cultivation, genetics, breeding and plant improvement and tissue culture. Other potential sources of diosgenin such as *Costus speciosus*, *Kallstroemia pubescens*, *Trigonella foenum graecum* and *Balavites aegyptiaca* have also been briefly described in this chapter. Chapter 3 incorporates different extraction and assay procedures of diosgenin and chapter 4 deals with conversion of diosgenin into various steroid drugs and their uses. Chapter 5 discusses other steroid drug precursors e.g., solasodine, hecogenin, stigmasterol, sitosterols, cholesterol, deoxycholic and cholic acids, ergosterol, vegetable pregnant steroids and miscellaneous precursors. Chapter 6 deals with production, requirement and trade of diosgenin and other steroid drug precursors.

The book contains three Appendices. In Appendix I the plant species reported to contain diosgenin have been mentioned ; glossary of botanical and agricultural terms have been incorporated in Appendix II and Appendix III mentions different diosgenin extraction centres in India.

The book has removed the long-felt need for a book containing all the aspects of diosgenin and other steroid drug precursors. Apart from the pleasing diagrams of different plant species including the tissue cultures, the structural formulae delineated in the book are neat. Nevertheless, it would have been better if the oldstyled structural formulae of diosgenin, solasodine and hecogenin were replaced by modern ones. Although the cover design is excellent, the binding of the book needs improvement. On the whole, it is an useful book fulfilling the aims set by the authors.

S. B. Mahato

NOTICE

Professor Alan R. Katritzky, FRS, has accepted appointment to the newly estabished Kenan Chair of Organic Chemistry at the University of Florida, Gainesville, and will be transferring there in August 1980. Under his guidance East Anglia has acquired a reputation for research in heterocyclic chemistry, spectroscopy and chemical education, and for international and industrial collaboration. There will be excellent opportunities for graduate students and post docs to work with him in Florida.

J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 765-768

Ligational Behaviour of a New Pyrazole-derived Tridentate : Mixed Ligand Complexes of Cobalt(II) with 1-Nitroguanyl-5-Methyl Pyrazole-3-Carboxylic Acid and Heterocyclic Amines

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Manuscript received 29 May 1979, revised 15 March 1980, accepted 21 May 1980

New mixed ligand complexes of cobalt(II) with 1-nitroguanyl-5-methyl pyrazole-3-carboxylic acid as the primary ligand and heterocyclic amines (as the co-ligand) have been prepared and characterised. The magnetic and electronic spectral features of metallic complexes are consistent with an average octahedral environment of the ligands around the central cobalt(II) ion and the ligand field parameters tacitly support such proposition. The i.r. spectra of the metal complexes indicate that the primary ligand is coordinated through the pyrazolyl nitrogen, the carboxylic oxygen and the nitrogen of the nitroguanyl group, thus showing tridentate (ONN) behaviour. The derivatographic studies have been useful in having an idea regarding the thermal stability and the mode of cleavage of the complex species.

PYRAZOLE-derivatives have long been acclaimed for their medicinal values and recently certain pyrazolo-pyrimidines are being studied in the fight against cancer[1]. The coordination chemistry of pyrazole-derived ligands has received much attention[2] in current years, primarily because of the biological importance of these heterocyclic bases which contain potential donor sites. However, most of the studies including recent work from our laboratory[3,4] have centred around synthesis and structural studies on the metal complexes of pyrazole containing bidentates. Till date, the only report of a pyrazole-derived tridentate, to our knowledge, is 1-(8-hydroxy 2-quinolyl)-3,5-dimethyl pyrazole[5] which has been proposed for the determination of cadmium by measuring the luminescence of the metal chelate. As a part of our programme devoted to a systematic study of the chelating tendencies of new pyrazole-based tridentates, we wish to report here the synthesis and structural characterisation (from magnetic, spectral and derivatographic studies) of cobalt(II) complexes with 1-nitroguanyl-5-methyl pyrazole-3-carboxylic acid (henceforth abbreviated as $NMPCH_2$), a potential tridentate, synthesised for the first time in our laboratory.

Experimental

All reagents used were of A.R. grade and the solvents were purified before use.

Preparation of the ligand ($NMPCH_2$) :

1-Nitroguanyl-5-methyl pyrazole-3-carboxylic acid was prepared by the condensation of sodium salt of ethyl acetopyruvate with nitro-aminoguanidine[6] following a method very similar to that adopted by Knorr and Macdonald[7] for the synthesis of 5(3)-methyl pyrazole-3(5)-carboxylic acid. The product on recrystallisation from hot ethanol produced a white crystalline compound, m.p. 189°. (Found : C, 33.80 ; H, 3.28 ; N, 32.86 ; $C_6H_7N_5O_4$ requires C, 33.70 ; H, 3.24 ; N, 32.82%).

Preparation of the mixed ligand complexes :

(a) Co(NMPC).$3H_2O$

Ethanolic solutions of hydrated cobalt(II) chloride (0.005 mole) and the ligand (0.005 mole) were mixed together. The resulting solution was adjusted to have $pH \approx 5$-6 by dilute ammonia solution ; the pink microcrystalline compound separated out within few minutes, this was filtered off, washed with water and alcohol and then dried over fused calcium chloride.

(b) Co(NMPC).B.$2H_2O$ (B = py, β-pico and γ-pico)

A solution of hydrated Co(II) chloride (0.005 mole) in ethanol was mixed with a solution of the ligand (0.005 mole) in the same solvent followed by the addition of the respective base to have *p*H of the reaction mixture around 5-6. The resultant compounds were collected as above.

(c) Co(NMPC). α-pico

The same preparative method outlined as in (b) was followed except that the reaction mixture was

refluxed to isolate the compound as shining deep pink crystals.

(d) Co(NMPC).B.nH_2O (B = bipy, *o*-phen, n = 2,3)

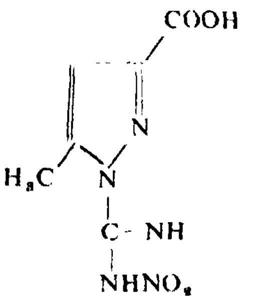
The resulting solution obtained by mixing ethanolic solutions of hydrated cobalt(II) chloride (0.005 mole) and the ligand (0.005 mole) was treated with ethanolic solution of the respective base (0.005 mole). To this was added dilute ammonia solution to have $pH \approx 5$-6 and then left at room temperature ($\sim 25°$) for about an hour. The microcrystalline compound separated, in each case, was collected as before.

Physical measurements and analyses :

The physico-chemical measurements like diffuse reflectance spectra, infrared spectra and magnetic susceptibilities in the solid state were carried out as described earlier[9]. The electronic solution spectra were taken on a Hilger-Watts UVISPEK spectrophotometer using DMF as solvent in a cell of 1 cm light path. Derivatographic analyses were done with the help of a Hungarian derivatograph [DERIVATOGRAPH ; System Paulik, F., Paulik, J. and Erdey, L., MOM (Budapest)]. The cobalt content in the complexes was determined gravimetrically as $CoSO_4$. C, H and N analyses were performed micro-analytically.

Results and Discussion

The condensation product of ethylacetopyruvate and nitroaminoguanidine is characterised as 1-nitroguanyl-5-methyl pyrazole-3-carboxylic acid(I) from elemental analyses and from a knowledge of the mode of formation of pyrazole derivatives[6].



(I)

The acid dissociation constants of the ligand, $NMPCH_2$, determined potentiometrically by Bjerrum method give values of $pk_2{}^* = 3.92$ and $pk_1^* = 8.96$ which correspond to the deprotonation from the carboxylic group and the nitroguanyl group respectively ; this fact indicates that the ligand has the potentiality of showing a diprotic (tridentate) function in forming metallic complexes at controlled *p*H values.

Magnetic and electronic spectral features :

Analytical data (Table 1) show the present mixed ligand complexes to conform to the general composition Co(NMPC).B.nH_2O (B = H_2O or N-heterocyclic base). The complexes are insoluble in water and in all the innocent organic solvents, but except the α-picoline adduct, they are fairly soluble in coordinating solvents like DMF, DMSO, etc.

TABLE 1—ANALYTICAL AND MAGNETIC DATA FOR THE COMPLEXES

Complex	Colour	Found(%)		Calc.(%)		μ_{eff}
		N	Metal	N	Metal	(B.M. at 304°K
Co(NMPC).3H_2O	pink	21.60	18.16	21.61	18.22	4.50
Co(NMPC).py.2H_2O	deep pink	21.93	15.33	21.82	15.32	4.52
Co(NMPC).α-pico	deep pink	23.08	16.12	23.14	16.26	4.76
Co(NMPC).β-pico.2H_2O	dirty pink	20.99	14.72	21.05	14.80	5.52
Co(NMPC).γ-pico.2H_2O	dirty pink	21.15	14.54	21.05	14.80	4.84
Co(NMPC).bipy.3H_2O	pink	20.26	12.37	20.40	12.29	5.14
Co(NMPC).*o*-phen.2H_2O	pink	20.27	12.16	20.08	12.09	4.85

The room temperature magnetic moments for the present cobalt(II) complexes lying between 4.50-5.14 B.M. are in some cases lower than those usually expected for high-spin octahedral cobalt(II) complexes. This lowering in magnetic moment values could be due to an orbital singlet ground state with a distorted octahedral stereochemistry of the complexes as is also supported by the electronic spectral data[10]. A small but perceptible increase in the moment values of the complexes Co(NMPC).B.2H_2O in the order of the coligated base (B) py$\leqslant\beta$-pico, $<\alpha$-pico, $<\gamma$-pico may be reconciled in terms of increasing basicity as well as increasing donor properties of these co-ligands in the same order[11].

In the reflectance spectra of the complexes, two principal bands located around 8500-10000 and 19000-21000 cm^{-1} may be assigned as a first approximation to the spin-allowed transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ respectively in an average field of octahedral(O_h) symmetry[12]. The split components of ν_3 (appearing as shoulders or very weak bands) may be attributed to the presence of low symmetry (approximating to C_2) components in the ligand field[13]. Using Ballhausen relationships[14] the ligand field parameters (Dq, B) have been calculated (Table 2). The B values (741-885 cm^{-1}) which are significantly less than the free ion (971 cm^{-1}) value, indicate considerable overlap and delocalisation of the d-orbitals of the metal. The calculated band positions for ν_2, using $\nu_2 = \nu_1 + 10Dq$ lie in the region 18180-19930 cm^{-1} (Table 2) and thus, only in case of Co(NMPC).py.2H_2O, the observed weak band near 18000 cm^{-1} may tentatively be attributed

TABLE 2—ELECTRONIC SPECTRAL BANDS AND LIGAND FIELD PARAMETERS OF THE COMPLEXES

Complex	Medium	Absorption maxima ν(cm^{-1})(ϵ)	ν_2 Calc.	ν_2 obs.	Dq (cm^{-1})	B (cm^{-1})	β^*
Co(NMPC).3H_2O	Reflectance	20400 ; 16400wsh , 9300	19810	—	1050	819	0.84
	DMF	20000sh(30.3) , 18180(26.6) , 16670sh(15.0)					
Co(NMPC).py.2H_2O	Reflectance	21800sh ; 20600 , 18000 , 9500wsh	18180	18000	968	885	0.91
	DMF	18520(24.5)					
Co(NMPC).α-pico	Reflectance	20500sh ; 19000 , 17400 , 9000	--	—	1011	741	0.76
Co(NMPC).β-pico.2H_2O	Reflectance	20000 ; 15800sh , 9200 ; 8700	19570	--	1037	796	0.82
	DMF	18690(25.5)					
Co(NMPC).γ-pico.2H_2O	Reflectance	20400 , 9300	19810	--	1050	819	0.84
	DMF	18520(25.2)					
Co(NMPC).bipy.3H_2O	Reflectance	20000 ; 16400wsh , 9300	19790	-	1048	790	0.81
	DMF	18180(27.0)					
Co(NMPC).o-phen.2H_2O	Reflectance	21400sh , 20200 ; 1300sh , 9400	19980	-	1058	799	0.82
	DMF	18520(26.2)					

$\beta^* = B/B_0 = B/970$ (B_0 = the Racah parameter value in the free ion state). C. K. Jorgensen, Advan. Chem. Phys., 1963, **5**, 33.

TABLE 3—SOME CHARACTERISTIC I.R. BANDS (4000-600 cm^{-1}) OF THE LIGAND ($NMPCH_2$) TOGETHER WITH THE COMPLEXES

Compound	N-H stretching mixed with O-H stretching	ν_{asy}(COO$^-$)	ν_{sy}(COO$^-$)	Coordinated water	Characteristic vibrations of secondary co-ligands
$NMPCH_2$	3340s 3170s	1720vs	1450s	—	—
Co(NMPC).3H_2O	3280sb	1600ms	1460w	875mb	—
Co(NMPC).py.2H_2O	3330sb	1620vs	1450s	885sb	1570ms ; 1480br ; 1460s
Co(NMPC).α-pico	3300sb	1610vs	1465ms	—	1565ssh ; 1480ms ; 1460s
Co(NMPC) β-pico.2H_2O	3280sb	1590vs	1470s	990m	1560ms , 1480ssh , 1480ms
Co(NMPC .γ-pico.2H_2O	3330sb	1640sb	1460ms	880sb	1580ms ; 1490s ; 1400ssh
Co(NMPC).bipy.3H_2O	3280sb	1610sb	1460s	870s	1440vs ; 1070ms ; 760s ; 730vs
Co(NMPC) o-phen.2H_2O	3330sb	1640sb	1450ms	885m	1430vs , 860sh , 780mb

s = strong ; v = very ; m = medium , b = broad , sh = shoulder.

to the ν_2 transition (in O_h). Moreover, this calculation does suggest that the shoulders around 16000-17000 cm^{-1} are not due to ν_2 transition and are likely to be the spin-forbidden transition $^4T_{1g}(F) \rightarrow {}^2T_{2g}(G)$[15]. The DMF solution of the complexes exhibits a main band around 18000-19000 (ν_3)($\epsilon < \sim 30$ cm^{-1}mole^{-1}) often accompanied with shoulders (Table 2) which might be taken as characteristic of distorted octahedral geometry. The shift of the absorption bands to lower frequency side as compared to the reflectance spectra suggest some sort of solvation.

I.R. Spectra :

The I.R. spectra (Table 3) in the present study proved to be of limited use in characterising the compounds due to the similarity of the ring systems, viz. the primary pyrazole ring and the secondary co-ligands py, pico, bipy, phen, etc. involved in complexation ; however difinite information has been gathered regarding the participation of carboxyl and nitroguanyl (-C=NH) group of NHNO$_2$ (attached to the C) $NMPCH_2$ in complex formation. All spectra (of the metal complexes show absorption characteristics of the aromatic ligands and all show absorption characteristics of the asymmetric (at 1590-1640 cm^{-1} as compared to 1720 cm^{-1} in the free ligand) and symmetric (1450-1470 cm^{-1}) ν_{COO^-} for coordinated carboxylate group attached to the pyrazole ring. The IR spectrum of the primary ligand, $NMPCH_2$, shows two strong bands at 3340 and 3170 cm^{-1} which are assigned to ν_{asy} (N-H) and ν_{sy}(N-H) modes of vibration respectively[16] of the nitroguanyl group ; these bands disappear and a strong broad band at ca. 3280-3330 cm^{-1} appears in the i.r. spectra of the metal complexes thereby suggesting deprotonation of one of the N-H groups in complexation forming nitrogen to metal bond[17]. However, the diffuse character and broadness of this band indicate inter or intramolecular hydrogen bonding between amide (=NH) group and H_2O molecules present in the complexes. The i.r. spectrum of Co(NMPC).3H_2O recorded down to 250 cm^{-1} shows one strong absorption in the region 310-320 cm^{-1} which is absent in the free ligand ; therefore it seems reasonable to assign this band to M-N (ring) stretching mode[18] giving positive indication of the pyrazole nitrogen being bonded to the metal ion ; this conclusion is in agreement with X-ray crystallographic studies of several pyrazole-metal complexes[19,20]. The characteristic vibration of the secondary co-ligands (py, pico, bipy, phen, etc.)

present (Table 3) in the metal complexes agree well with those reported earlier showing their coordinated nature in the corresponding adducts[21,22]. Moreover, the hydrated complexes, Co(NMPC).B.$2H_2O$ (B = H_2O, py, β or γ-picoline) show an additional band around 880-990 cm^{-1} characteristic of the rocking mode of coordinated water[23] while the absence of any such band in the spectra of bipyridyl and phenanthroline adducts indicates that water molecules are not coordinated in these species; the results of thermal analyses (see below) of the compounds also support this proposition.

Derivatographic studies :

The DTG and DTA peaks in the derivatograms of the primary ligand ($NMPCH_2$) and the complex species indicate in a stepwise manner the loss of water (both coordinated and lattice water molecules at different temperatures) and secondary base molecules followed by simultaneous decarboxylation and loss of the nitroguanyl group; however, except the anhydrous species none of the intermediates could be isolated. The final conversion of the complex species to cobalt oxide is complete around 450°.

Conclusion :

It appears, therefore, that the ligand 1-nitroguanyl-5-methyl pyrazole-3-carboxylic acid ($NMPCH_2$) functions as a diprotic (ONN) tridentate in forming the present Co(II) complexes coligated with either water molecule or heterocyclic amines; in general the seemingly pentacoordinate monomeric complex species (as evidenced from i.r. and thermal analysis) appear polymeric octahedral having approximating C_s-symmetry (as evidenced from electronic spectra) where the polymerisation might be effective through additional bonding sites of either the nitroguanyl or the carboxyl group of the primary ligand molecule.

Acknowledgement

The authors are thankful to Prof. S. E. Livingstone of the University of New South Wales, Australia, for providing them with the diffuse reflectance spectra of the complexes. The authors are also thankful to Dr. S. N. Poddar of IACS, Calcutta for derivatographic analyses of the complexes.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 769-772

Preparation and Characterisation of Potassium-*bis*(salicylato)diaquotitanium(III) dihydrate and *bis*(salicylato)diaquomanganese(II)

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Manuscript received 25 January 1979, revised 20 March 1980, accepted 19 May 1980

Potassium *bis*(salicylato)diaquotitanium(III) dihydrate and *bis*(salicylato)diaquomanganese(II) complexes have been prepared by mixing metal hydroxide and aqueous solution of ligand in 1 : 2 molar ratio. The complexes have been characterised by elemental analysis, derivatographic study (D.T.G., D.T.A., T.G.A.), i.r. spectra measurements, magnetic susceptibility measurements, U. V. and visible reflectance measurements in solid phase. In the case of *bis*(salicylato)diaquomanganese(II) e.s.r. and preliminary X-ray data are also presented.

THE literature survey reveals that the salicylato complexes of many metals including titanium and manganese have been prepared by a number of workers[1-6] with conflicting results. None of these studies have suggested their structures. In this paper we are reporting the preparation and characterisation of potassium *bis*(salicylato)diaquotitanium(III) dihydrate and *bis*(salicylato)diaquomanganese(II) by derivatographic study, i.r. spectra, magnetic susceptibility and U.V. and visible reflectance measurements in solid phase. In case of Mn-complex e.s.r. and preliminary X-ray diffraction data have also been presented.

Experimental

Methods :

Potassium *bis*(salicylato)diaquotitanium(III) dihydrate was prepared by the interaction of freshly prepared $Ti(OH)_3$ and salicylic acid (1 : 2 metal ligand ratio). The *p*H of the solution was adjusted to 6-7 by the addition of dil. KOH solution. *Bis*(salicylato)diaquomanganese(II) was prepared by the interaction of $MnCO_3$ and salicylic acid (1 : 2 metal ligand ratio). The obtained solution in both the cases was allowed to evaporate in air. After a few days brilliant golden yellow and light buff crystals were obtained respectively in the case of titanium and manganese. The percentage of titanium and manganese was determined as TiO_2 and $MnSO_4$ respectively[7]. Carbon and hydrogen have been estimated by element estimation technique. Potassium was estimated by flame photometer.

Instrumental :

The derivatographic study were made on a system of Paulik, Paulik and Erdey[8] manufactured by M/s. M.O. M. (Hungarian Optical Works). For D.T.A. ignited alumina has been used as the inert material.

The i.r. spectra were recorded on a Perkin-Elmer Model No. 221. Magnetic susceptibility of the complexes were measured on a Gouy balance at room temperature. The spectrophotometric study was carried out on Hilger and Watts Uvispeck spectrophotometer Model No. 700. The silika prism and higler Uvispeck standard reflectance attachment was used to measure the reflectance spectra of the solid complexes. Branker Physic Model BER 402 operated in X-bend using 100 K_c modification frequency was employed for e.s.r. spectra measurements.

For X-ray diffraction analysis good single crystal was selected by observing extinction under a polarised microscope. Oscillation, rotation and Weissenberg photographs were taken with CuK_α radiation to determine unit cell, space group and cell contents.

Derivatographic Study :

The combined D.T.G., D.T.A. and T.G.A. study of a sample of 600 mg of potassium *bis*(salicylato)-diaquotitanium(III) dihydrate and *bis*(salicylato)-diaquomanganese(II) were carried out with heating

Found				Calculated	Calculated			
K	M	C	H	for	K	M	C	H
9.5%	11.01%	38.12%	3.9%	$K[Ti(OC_6H_4COO)_2(H_2O)_2]2H_2O$	9.05%	11.14%	38.75%	3.71%
	14.98%	45.54%	4.05%	$[Mn(OHC_6H_4COO)_2(H_2O)_2]$		15.07%	46.05%	3.84%

rate of 8°/min in static air. The temperature was fixed between 30° to 800°. The summary of the result are in Tables 1 and 2

TABLE 1—POTASSIUM *bis*(SALICYLATO)DIAQUOTITANIUM(III) DIHYDRATE $K[Ti(OC_6H_4COO)_2(H_2O)_2]2H_2O$

Position of peak in D.T.G. curve	Compound formed and weight in T.G.A. curve	Nature of peak in D.T.A. curve position of inflexion point
60°-125°	$K[Ti(OC_6H_4COO)_2(H_2O)_2]$ 551 mg	Endo at 120°
120°-210°	$K[Ti(OC_6H_4COO)_2]$ 510 mg	Endo at 210°
245°-280°	Product not known-485 mg	Endo at 260°
280°-370°	$(K_2CO_3)_{\frac{1}{2}}[TiO(OC_6H_4COO)]$ 375 mg	Endo at 315°
		Exo at 335°
370°-460°	$\frac{1}{2}(K_2CO_3)_{\frac{1}{2}}(TiOCO_3)$ [illegible] mg	Endo at 425°
460°-640°	$\frac{1}{2}(K_2CO_3)\frac{1}{2}TiO_2$ 215 mg	Endo at 510°
		Exo at 550°
		Endo at 630°
		Exo at 640°
640°-730°	$[\frac{1}{2}K_2O+TiO_2]$ 179 mg	Endo at 730°
730°-770	$[KTiO_{2.5}]$ 179 mg	Exo at 770°

TABLE 2—*Bis*(SALICYLATO)DIAQUOMANGANESE(II) $[Mn(OHC_6H_4COO)_2(H_2O)_2]$

Position of peak in D.T.G. curve	Compound formed and weight in T.G.A. curve	Nature of peak in D.T.A. curve and position of inflexion point
135°-185°	$[Mn(OHC_6H_4COO)_2]$ 540 mg	Endo at 170°
240°-320°	$[Mn(OC_6H_4COO)]$ 310 mg	Endo at 290°
390°-510°	$MnCO_3.MnO$ 134 mg	Exo at 375°
		Endo at 500°
510°-670°	MnO 115 mg	Exo
670°-700°	Mn_3O_4 120 mg	Exo

Endo = Endothermal peak, Exo = Exothermal peak.

I.R. Spectra :

The i.r. spectra of $K[Ti(OC_6H_4COO)_2(H_2O)_2]$-$2H_2O$ and $[Mn(OHC_6H_4COO)_2(H_2O)_2]$ were taken in nujol mull. The i.r. spectra of both the complex displays a broad and medium band of 3480-3400 cm^{-1} and 3450-3250 cm^{-1} attributed to ν(OH) vibration of water molecule. The HOH deformation vibration of water molecule expected near 1600 cm^{-1} is sometimes involved in the strong ν(CO) vibration of coordinated carboxylic group. A new and medium band in i.r. spectra of almost both the complexes near 810 cm^{-1} suggest the coordination of the water molecule.

The i.r. spectra of $K[Ti(OC_6H_4COO)_2(H_2O)_2]$-$2H_2O$ displays ν_{as}(CO) vibration at 1590 cm^{-1} and ν(CO) vibration at 1340 cm^{-1}. The splitting of ν_{as} (C=O) and ν_s(C=O) could not be located in this complex. The decrease in the i.r. vibration of phenolic(C–OH) 1230 cm^{-1} and ν(CO) vibration in the complex suggests the bonding of both the carboxylic oxygen and phenolic oxygen in the complex. The compounds also show two sharp bands at 885 cm^{-1} and 832 cm^{-1} which may be due to Ti–O stretching[9,10]. A strong band at 632 cm^{-1} may also be attributed to ν(Ti–O) vibration.

The i.r. spectra of $[Mn(OHC_6H_4COO)_2(H_2O)_2]$ displays the splitting of bands at 1145, 1240 and 1300 cm^{-1}. These indicate the presence of free phenolic-OH.

This is also confirmed by chemical tests. The ν_{as}(CO) vibration shifts to lower frequency and is observed at 1585 cm^{-1}. The ν_s(CO) bond due to carboxylate group is found to occur at 1382 cm^{-1} and 1342 cm^{-1}. Thus it is inferred that carboxylate group of coordinated salicylate anion is involved in bidentate bonding through the both oxygen atoms. The phenolic-OH is probably not coordinated to Mn(II) as (C–OH) vibration remains uneffected in the complex.

Magnetic Susceptibility measurements, U.V. and Visible Reflectance spectra and e.s.r. spectra :

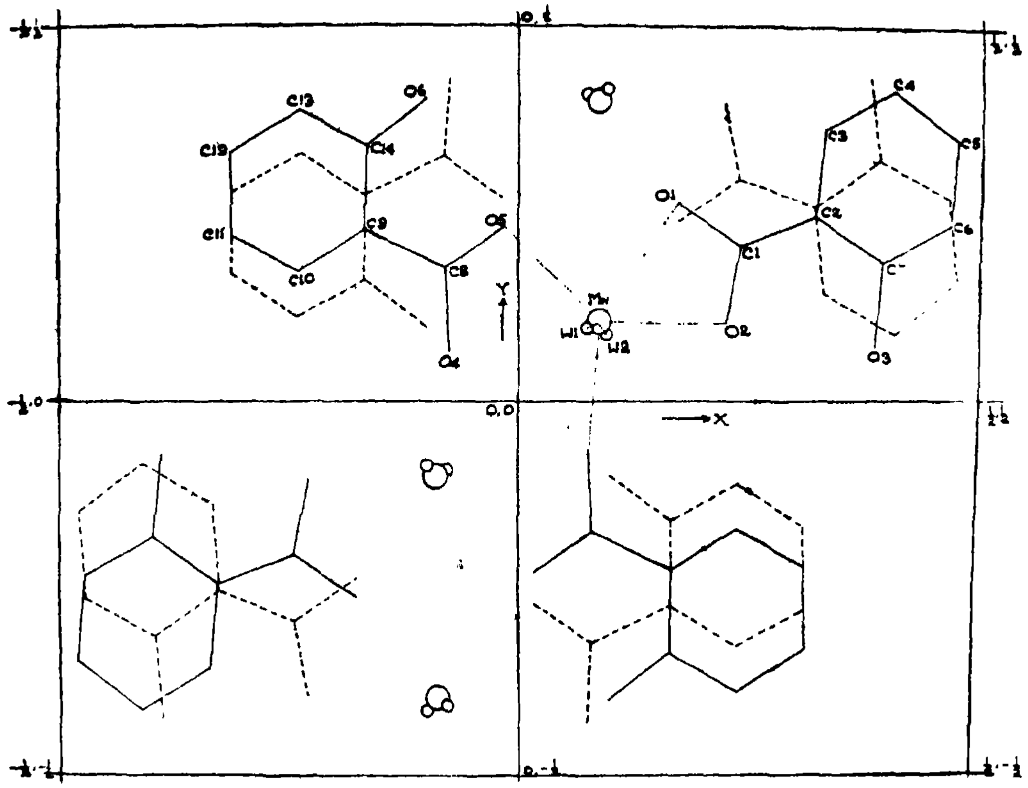
The magnetic moment value for $K[Ti(OC_6H_4$-$COO)_2(H_2O)_2]2H_2O$ was found to be 1.92 B.M., which corresponds with magnetic moment value for one unpaired spin. This moment value definitely suggests that complex contains Ti in Ti^{3+} state. The magnetic moment value for $[Mn(OHC_6H_4COO)_2$-$(H_2O)_2]$ has been found to be 5.98 B.M. and therefore the complex possesses high spin octahedral environment around manganese(II).

U.V. and visible reflectance spectra was recorded in the region 350 to 1000 nm. In case of $[Ti(OC_6$-$H_4COO)_2(H_2O)_2]2H_2O$ no distinct band could be observed rather a shoulder was observed to 460 nm. This band is assigned to $^2T_{2g} \longrightarrow E_g$ band in octahedral field. $[Mn(OHC_6H_4COO)_2(H_2O)_2]$ did not show any band in this region.

The e.s.r. spectra of the complex $[Mn(OHC_6$-$H_4COO)_2(H_2O)_2]$ was recorded and the g value was calculated to be 2.08 [using D P P H (g = 2.0036) as a standard]. This g value is expected for six coordinated spin free octahedral manganese(II) complexes.

X-ray Analysis :

The X-ray structure of the compound *bis*-(salicylato)diaquomanganese(II) has been investigated. The crystal was found to be monoclinic with following cell parameters $a = 15.64_6$ Å, $b = 12.34_6$ Å, $c = 7.26$ Å, $\alpha = \gamma = 90°$, $\beta = 96.9°$. Unit cell volume 1392.28 $Å^3$ No. of formulae within the unit cell Z = 4, Space group $P_{2_1/c}$. The cell content of the unit cell was calculated from the relation $\rho = \frac{1.66 \times Mz}{V}$



where ρ = density in gm cm^{-3}, M = mol wt of the formula, Z = formula within the unit cell, V = vol of the unit cell in $Å^3$.

The density of the crystal was determined by flotation method using a mixture of bromoform and toluence. The observed density was found to be 1.73 cm^{-3} which gives a volume of unit cell content Mz = 1451.7.

The calculated density assuming Z = 4 comes to be 1.74 cm^{-3} which is in excellent agreement with the observed density.

The unit cell contains four units of the formula $[Mn(C_6H_4OHCOO)_2(H_2O)_2]$. The structure of the compound was determined by three-dimensional X-ray diffraction data by heavy atom technique. The metal ion occupies the space position 0, 0, 0 and 0, 1/2, 1/2. Here the metal is linked with six oxygen atoms as shown in figure. The metal and oxygen bond-distance are indicated as below :

$Mn\text{-}O_4 = 2.12Å$, $Mn\text{-}W_2 = 2.15$, $Mn\text{-}O_2 = 2.13$,

$Mn\text{-}O_5 = 2.20Å$, $Mn\text{-}W_1 = 2.38$, $Mn\text{-}O_1 = 2.30$

The X-ray result indicates that in this complex both the O-atom of carboxylic gr. is attached by metal atom. Phenolic-OH gr. is free, other two oxygens are of water molecule denoted by W_1 and W_2. The two different molecules are joined by the O-atom of carboxylic group as shown in figure.

Acknowledgement

The authors wish to express their thanks to Dr. L. K. Mishra, Dept. of Chemistry, Patna University for his valuable suggestions in the preparation of manuscript. Dr. M. P. Gupta, Head of Department Physics, Ranchi University, Ranchi for X-ray analysis, Director, P.R.W. (P&D) Sindri for e.s.r. spectra and Director, C.F.R.I., Dhanbad for i.r. spectra and derivatographic study.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 773-774

Quaternary Alkaloids of *Tiliacora racemosa* Colebr*.

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Manuscript received 26 March 1979, revised 19 February 1980, accepted 21 May 1980

Magnoflorine, lotusine and magnocurarine chlorides have been isolated from the leaves, stems and roots of *Tiliacora racemosa* Colebr. These quaternary bases have been found responsible for curarizing action and hypotensive activity of the water soluble alkaloidal fraction of the plant.

TILIACORA racemosa Colebr. (Menispermaceae) an evergreen climbing shrub, grows throughout the tropical regions of India. The plant has been extensively investigated for its alkaloidal constituents and a number of interesting alkaloids have been isolated and fully characterised[1-5]. Reports of isolation of a number of uncharacterized tertiary and quaternary bases from *T. racemosa* are also on record[6,7].

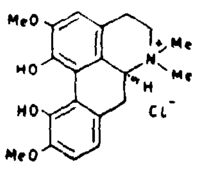
During a screening programme on biological activities of Indian medicinal plants, hypotensive, neuromuscular blocking and spasmolytic activities were observed in 50% ethanolic extract of *T. racemosa*[8] The characterization of the quaternary bases responsible for curarizing action and hypotensive activity of the ethanolic extract of the plant is reported in the present communication.

Experimental

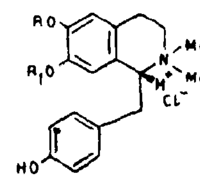
The quaternary bases present in the aqueous solution were precipitated as their reineckates[9,10]. Careful chromatography of the mixture of quaternary bases on cellulose column furnished the following alkaloids. Alkaloid A($C_{20}H_{24}O_4NCl$), m.p. 208-210° (decomp); Alkaloid B($C_{19}H_{24}O_3NCl$), m.p. 213-215° (decomp) and Alkaloid C($C_{19}H_{24}O_3NCl$), m.p. 150-152° (decomp).

The IR (ν_{max}^{KBr} 3255, 1604 and 1238 cm^{-1}) and UV (λ_{max}^{EtOH} 231, 272 and 308 nm and $\lambda_{max}^{EtOH-NaOH}$ 315 nm) spectra of alkaloid A suggested the presence of an aporphine system substituted at 1, 2, 10 and 11 positions[11]. In the NMR spectrum the aromatic methoxyl groups at C-2 and C-11 appeared together at τ6.32. In the aromatic region of the spectrum there were three protons. Of these one proton singlet at τ3.22 was due to C-3 proton. The remaining two protons at C-8 and C-9 resonated together at τ3.01. The absence of characteristic low field C-11 aromatic proton in the spectrum of alkaloid A confirmed that the base is a representative of 1, 2, 10, 11-tetra-substituted aporphines[12]. A singlet for six protons at τ5.65 was due to $\overset{+}{N}-(CH_3)_2$ group. The data presented above revealed close similarity of alkaloid A with magnoflorine chloride[13](*1*). Direct comparison with authentic sample established the identity.

The IR spectrum of alkaloid B (ν_{max}^{KBr} 3155, 1605 and 1240 cm^{-1}) in conjunction with its UV data (λ_{max}^{EtOH} 282 nm and $\lambda_{max}^{EtOH-NaOH}$ 295 nm) suggested the presence of 1-benzyltetrahydroisoquinoline system[14] in the base. In the NMR spectrum of alkaloid B, a sharp singlet for one proton at τ4.35 was assigned to C-8 aromatic proton. A singlet for one proton at τ3.30 was due to C-5 aromatic proton. A sharp singlet for three protons at τ6.72 was assigned to C-7 methoxyl group which is known to resonate at a higher field due to conformational reasons[15-17]. In the aromatic region an A_2B_2 quartet for four aromatic protons at τ3.05 and 3.25 (J=8 Hz) was due to a *para*-substituted benzyl moiety. Two sharp singlets each of three protons at τ6.60 and 6.88 were assigned to $\overset{+}{N}-(CH_3)_2$ group. The structure (*2*) of lotusine chloride[17] emerged for alkaloid B from the spectroscopic data



(1)



(2) R=H; R1=Me
(3) R=Me; R1=H

presented above. Direct comparison of alkaloid B with lotusine chloride established the identity.

The IR spectrum of alkaloid C (ν_{max}^{KBr} 3500, 3411, 1603 and 1235 cm^{-1}) in conjunction with its UV

* C. D. R. I. Communication No. 2546.

data (λ_{max}^{EtOH} 285 nm and $\lambda_{max}^{EtOH-NaOH}$ 299 nm) suggested the presence of 1-benzyltetrahydroisoquinoline system[14]. The NMR spectrum of alkaloid C was more informative. A sharp singlet for one proton at τ3.82 was due to C-8 aromatic proton. A sharp singlet for one proton at τ3.11 was assigned to C-5 aromatic proton. A sharp singlet for three protons at τ6.01 was due to C-6 methoxyl group. Four aromatic protons of *p*-substituted benzyl moiety appeared as a multiplet centered at τ3.09. Two sharp singlets each for three protons at τ6.50 and 6.75 were assigned to $\overset{+}{N}(CH_3)_2$ group. The physical constants and spectroscopic data of alkaloid C were very close to the reported data of magnocurarine chloride[18](*3*) isolated from *Colletia spinosissima* Gmel. Direct comparison with authentic sample established the identity.

Biological Activity :

Alkaloids A, B and C, isolated from the water soluble alkaloidal fraction of *T. racemosa* and characterized as magnoflorine, lotusine and magnocuranine chlorides respectively, showed d-tubocurarine like curarizing action on the sciatic skeletal muscles as reported earlier[8]. These quaternary bases also induced hypotensive effects in dog, cat and rabbit. This myoneural transmission inhibitory activity is believed due to ganglionic blocking action of these drugs on various sympathetic and parasympathetic ganglia.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 775-778

A Study of Fluorescein as a Ligand. Part—VI

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Manuscript received 27 November 1979, accepted 25 December 1979

Fluorescein has been investigated as a ligand and oscillator strengths have been calculated, from spectral data, in acidic media as well as in various pH ranges.

FLUORESCEIN was first prepared by Baeyer as back as in the year 1871 and assigned a lactoid structure. Kopp and Decker[6] and Pope *et al*[7] gave cogent reasons for a *p*-quinoid structure to the molecule. Orndroff[8] has shown that fluorescein exists in two isomeric forms, red and yellow, the latter with a lactoid and former with *p*-quinoid one. The present authors undertook a study of fluorescein under two aspects, (i) to study it as a ligand for the complexes already reported [1-5] and adducts to be reported[9] and (ii) to determine the oscillator strengths in various media.

Experimental

Fluorescein was obtained from B.D.H., Poole (England) and was purified by dissolving in a strong solution of NaOH and precipitating it fresh by Analar HCl. The elemental analysis is given below :

Analysis :

Found : C, 72.28 ; H, 3.71 ; Calculated for $C_{20}H_{12}O_5$ C, 72.30 ; H, 3.60.

The red crystalline sample, so obtained, was found to dissolve sparingly in methanol, ethanol, acetic acid, nitrobenzene and formic acid. It dissolved readily in hot aniline, formic acid and acetone.

Spectra were recorded on an automatic and range adjustable Pye-Unicam SP 8-100 Spectrophotometer which was previously checked and adjusted by a dydimium glass spectrum. Diffuse reflectance spectra were recorded with the special attachment to SP-500 by disc method, MgO being the standard.

Infra-red wavelengths were obtained on Perkin-Elmer 137-1281 Infracord. Both the KBr pellet technique and the nujol mull method were employed.

* Senior author to whom all correspondence should be directed.

The magnetic measurement of the samples were taken on a simple Guoy balance at room temperature.

Results and Discussion

The electronic absorption spectral data of fluorescein is given in Table 1 and the characteristic wave numbers (cm^{-1}) in the I.R. spectrum of the sample with probable assignments are given in Table 2.

TABLE 1—ELECTRONIC ABSORPTION SPECTRA OF FLUORESCEIN

Solvents	Dielectric constant (ε)	$\lambda_{(max)}$ nm	log E_m
Formic acid	58.52	391, 397	3.36, 2.76
Nitrobenzene	34.81	409, 452	2.84, 3.27
Methanol	32.58	451, 491	2.96, 3.22
Ethanol	24.30	458, 487	3.09, 3.71
Acetic acid	6.19	412(sd)400-460	4.22
Solid diffuse reflectance	—	397, 401, 462	—

TABLE 2—INFRA-RED DATA FOR FLUORESCEIN AND ASSIGNMENTS

$\bar{\nu}$, cm^{-1}		Assignment
705	B.M	
755	B.W	
846	Sd S	
862	B.M	
920	B.M	OH out of plane bending of acid dimer
1110	S	Symmetric stretching C – O – C
1204	S	(i) Antisymmetric C – O – C stretching, (ii) C – O stretching in phenolic OH
1235	S	C – O stretching
1255	S	(i) O – H in plane bending, (ii) C – O stretching
1300	S	(i) Coupling between OH bending and CO stretching in acid dimer, (ii) aromatic ether
1375	S	(i) OH deformation, (ii) aromatic ring
1400	Sd M	(i) Symmetric COO stretching, (ii) Coupling between OH bending and CO stretching of acid dimer
1452	S	Aromatic ring
1472	S	
1588	V.S	(i) Antisymmetric COO stretching, (ii) Aromatic ring
1625	Sd M	Quinoid carbonyl or aromatic ring
1675	B.W	(i) Associated carboxyl group, (ii) Quinoid carbonyl
3000-300B		OH stretching

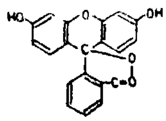
The spectral data of fluorescein is extensive but the recorded results show wide variations[10-12]. But in all these investigations, the solutions of fluorescein were made in alkaline media of different strengths. Long time back, Meyer and Fischer[13] have shown that even a violet coloured solution of fluorescein in boiling alkali gave a spectrum similar to that of normal alkali solutions. Visible and ultraviolet region of the spectrum of alkaline and neutral solutions of fluorescein were studied by Medhi and Watson[14], and Howe[15]. Among other workers who studied the spectra, mention may be made of the work of Formanek and Knop[16] and Holmes[17]. Moir[18] studied the visible spectrum of the dye in concentrated sulphuric acid. From the scrutiny of spectral data, it is evident that the results are not concordant. The reason may be that either the dye that was used was too much of a commercial type or the method of instrumentation had not reached that perfection to give accurate results.

It is known that fluorescein exists in two physical modifications—red and yellow. It is usual to ascribe the quinoid form to red variety and lactoid structure to the yellow one. According to Orndroff[19], both give identical absorption spectra in a number of solvents and hence both exist in solution in the quinoid state. These very workers took reflectance spectra of another form of fluorescein-bright yellow-crystallised from pyridine solution and found no distinct characteristics of this form. They recorded the absorption spectra of the dye in concentrated sulphuric acid, 75% formic acid and alçoholic solution of HCl and came to the conclusion that in each case fluorescein exists as a salt of the respective acid.

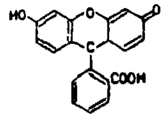
Baeyer[20] studied a solution of fluorescein in strong boiling alkali spectrophotometrically and predicted a possible rupture of pyrone ring with the formation of tetrabasic salts. Meyer and Fischer[21] detected a reasonable resemblance between the absorption of phenolphthalein in weak alkaline solution and that of fluorescein in hot strong alkali. Lewis and Kasha[22] have estimated the energy of the phosphorescent state of fluorescein to be 51 K cals higher than the normal singlet state. They have also demonstrated that the phosphorescent triplet state is paramagnetic[23].

The spectral data recorded by the present workers in Table 1 shows the characteristic spectral maxima of the dye in various solvents such as formic acid, methanol, etc. and log ϵ_m values. It is clear that the state of fluorescein molecule is apparently different in different solvents and there is a marked "blue shift" as the dielectric constant (ϵ) of the solvent increases.

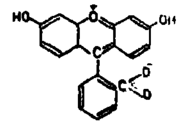
The infrared lines have to be inspected in the light of three alternative structures as suggested by Davies *et al*[24] in their infra-red studies of the molecule (I, II and III).



I



II



III

The present authors eliminate structure(II) temporarily on the ground that the solid did not show characteristic intense associated carboxyl group absorption extending from 3500-2500 cm^{-1} (Table 2). Besides, they did not observe expected strong absorption near 1630 cm^{-1} due to associated carboxylic and quinoid carbonyl groups in structure(II). However, the expected absorption for the lactoid structure for fluorescein molecule is clearly obtained near 1730 cm^{-1}. Structure(III) is easily eliminated because the strong characteristic frequencies for carboxylate ion (CO$\bar{O}$) namely 1560 and 1430 cm^{-1} are completely absent. Yet another reason, why the present authors do not choose structure (III), is that it hints at paramagnetic susceptibility of the fluorescein, whereas actually on a Gouy magnetic balance, the authors measured the susceptibility of both red and yellow variety to be $-.48$ c.g.s.u., a distinctly diamagnetic moiety. Again, the separation of charges between two oxygen centres, in structure (III), also would appreciably reduce the contribution of the structure to the actual state of molecule.

Davies *et al*[24], on the basis of their infra-red absorption studies of phenol, phenolphthalein, fluorescein and some alkali derivatives of it, have assigned the lactoid structure (I) to fluorescein.

If now one examines the I.R. data (Table 2) critically, the absorption observed at 1675 cm^{-1}, which may be assigned to associated carboxyl group or/and the quinoid carbonyl group, lends partial support to the quinoid structure[25]. The broad absorption bands near 920 cm^{-1} and 2500-3500 cm^{-1} also indicate the probable presence of an associated carboxyl group. One of the authors (R.A.B.) used deep red coloured fluorescein for complex studies[1-5] and this colour suggests a quinoid rather than a lactoid structure.

When one examines the fluorescein molecules, it is found that it possesses coordinating oxygen atom at three positions namely, in the carbonyl group, the hydroxyl group and the carboxyl acid group. Because of the presence of C=O, C–O and OH group in more than one environment in the fluorescein molecule, the task of assigning a particular frequency to a particular group in the metal complexes of fluorescein[1-5] is difficult. The infrared spectra of the metal complexes of fluorescein[1-5], in general, show a definite displacement of OH and

C – O frequencies indicating a specific co-ordination through the OH and C – O linkage in the fluorescein molecule. It is well known that fluorescein forms a disodium salt with replacement of hydrogen atoms in the hydroxyl and the carboxyl groups by sodium atoms. It is, therefore expected that in the case of metal complexes which have been formed under alkaline *pH* conditions 1-5, there is a distinct possibility of the carboxyl group taking pårt in the complex formation with metal ions.

Oscillator strengths of fluorescein :

Oscillator strengths of fluorescein have been previously investigated[26–28] but the solvents employed were not of wide range. The present authors have used same seventeen media to come to a final conclusion regarding oscillator strengths and the method of measurement adopted was the same as mentioned by Jorgensen[29] as well as his method of calculations. The spectra of fluorescein in various media have not been presented here but the essential details have been set out in Table 3. The

TABLE 3—RELEVANT DATA FOR THE OSCILLATOR STRENGTHS OF FLUORESCEIN MOLECULE

Solvent of Medium	$\lambda_{m(nm)}$	$\epsilon_{max} \times 10^4$	h(cm^{-1})	*f*
1*M* H_2SO_4	440	2.96	26580	3.518
2.06*M* H_2SO_4	438	3.10	14620	2.027
3.2*M* H_2SO_4	436	3.10	7790	1.095
6.1*M* H_2SO_4	434	4.80	4800	1.040
7.2*M* H_2SO_4	433	5.80	5580	1.452
9.02*M* H_2SO_4	431	6.60	5410	1.580
0.2*M* $HClO_4$	460	1.20	6540	0.3570
0.021*M* $HClO_4$	461	0.98	6790	0.3060
0.126*M* H_2SO_4	461	1.10	6600	0.3246
$KH_3(C_2O_4)_2.2H_2O$ (Buffer *p*H 12.15)	438	0.80	10930	0.3910
Succinate of Sodium Buffer *p*H = 5.4	484	0.73	4110	0.1342
Phosphate of K & Na Buffer *p*H = 8.9	486	0.69	6160	0.1901
Borax Buffer *p*H = 9.18	489	0.66	4640	0.1370
Na-Carbonate Bicarbonate Buffer *p*H = 10.0	494	0.58	29040	0.7532
Acidphthalate Buffer *p*H = 2.09	480	0.76	7930	0.2696
Acetic acid Buffer *p*H = 4.638	462	0.77	29860	1.028
HCl-KCl Buffer *p*H = 2.09	439	0.91	4250	0.1780

symbols ϵ_{max}, h, f and λ have the usual meanings. The oscillator strengths of fluorescein anion reported by Rohatgi[28] fall in the range ~0.60 whereas the reported values of *f* in the present work, range from 3.5 (1 *M* H_2SO_4) to 0.13 (for *p*H 5.4). Oster and Adelman[30] report that the ϵ_{max} of sodium salt of fluorescein, eosin, is 7.25×10^4 1/mole whereas the $\int \epsilon d\nu$ is of the order of 7.84×10^8 1/mole sec. The present work, in the buffer region shows this to be a slightly erroneous conclusion, however the $\int \epsilon d\nu$ values seem to generally agree. The conclusions are inevitable, in the light of work by Gilman *et al*[31] and Orndorff *et al*[32], that is, in the acidic range of 1*M* H_2SO_4, a neutral molecule of fluorescein exists and changes to triplet state monocation in subsequent dilutions of sulphuric acid. In the *p*H range of 5.4 to 10.0 the state of fluorescein is divalent anion. This agrees, to some extent, with the work reported by Lindquist[33] and Cordier and Grossweiner[34]. They have come to the conclusion, by flash photolysis and pulse radiolysis methods, that at 355 nm, semireduced monoanion, at 394 nm, semireduced dianion, and at 428 nm semioxidised monoanion are formed from fluorescein molecule.

Acknowledgement

One of the authors (L.P.) thanks the Professor and Head, Department of Chemistry, Dr. K. A. Thakar for allowing her to use the facilities in the department for her post-doctoral work.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 779-782

Studies on the Citrate Complex of Dimethyl Tin

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Manuscript received 5 August 1974, accepted 24 July 1975

The complex formation of dimethyl tin with the citrate ligand has been studied by the *p*H titration method. The formation of a 1 : [illegible] type of complex is reported. A neutral complex (C) is formed below *p*H 3.4 which behaves like a tribasic acid and dissociates to complexes C_1^-, $C_2^=$ and C_3^{3-} and protons at higher *p*H. The equilibrium constants of the reactions,

$$(CH_3)_2Sn^{++}+H_3Cit \rightleftharpoons C+2H^+,\ C \rightleftharpoons C_1^-+H^+,\ C_1^- \rightleftharpoons C_2^=+H^+ \text{ and } C_2^= \rightleftharpoons C_3^{3-}+H^+$$

are found to be 2.29×10^{-6}, 6.31×10^{-4}, 5.48×10^{-6} and 5.28×10^{-6} respectively.

YASUDA and Tobias[1,2] have studied the complex formation of picolinic acid and phenanthroline with dimethyl tin. Since the citrate complex of this cation has not yet been studied, we thought it worthwhile to investigate this system.

Experimental

Four *p*H titrations were performed to investigate the complex formation. *p*H titrations were carried out by a Marconi *p*H meter (TF 1093/1) at 28°. The ionic strength is kept constant at 0.1*M* by the addition of potassium chloride. The dimethyl tin dichloride solution is prepared by dissolving a known amount of dimethyl tin dichloride in a known amount of hydrochloric acid solution to suppress the hydrolysis. This amount of acid is neutralised by KOH after the addition of citrate ligand. The experiments were carried out in nitrogen atmosphere.

Results and Discussion

The liberation of protons during the complex formation remains same when the metal to ligand ratio is increased from 1 : 1.25 to 1 : 5. The nature of the curves are also similar in both 1 : 1.25 and 1 : 5 ratio systems. This indicates the formation of a 1 : 1 type of complex. The horizontal distance increases in the beginning and then remains nearly constant upto *p*H 6.0 and then increases.

The reaction taking place in the experiment (I) can be represented as

$$(CH_3)_2Sn^{++}+H_3Cit \rightleftharpoons C+nH^+ \qquad (1)$$

$$K_1=\frac{[C][H^+]^n}{[(CH_3)_2Sn^{++}][H_3Cit]} \qquad \ldots (1\text{-}i)$$

where C is the dimethyl tin citrate complex. The equilibrium constant is given by the equation (1-i).

It can be shown as in the case of cadmium citrate complex[3], yttrium citrate[4] and yttrium tartrate[5] complex that

$$\frac{\Delta[NaOH]-\frac{a}{b}\Delta[Ct]}{[C]}=n-\frac{a}{b} \qquad (2)$$

when the formation of the complex is complete

$$[C]=[(CH_3)_2SnCl_2]$$

Hence,

$$\frac{\Delta[NaOH]-\frac{a}{b}\Delta[Ct.]}{[(CH_3)_2SnCl_2]}=n-\frac{a}{b} \qquad \ldots (2\text{-}i)$$

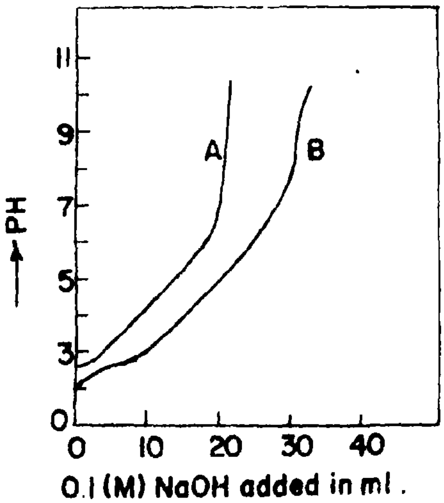


Fig. 1. *p*H titration of 100 ml of solution containing 0.000625 g moles of citric acid and 0.01 g moles of KCl (Curve A) and that of the same volume of another solution containing same quantity of the above constituents and 0.0005 g moles of dimethyl tin dichloride (Curve B) against 0.1*N* sodium hydroxide.

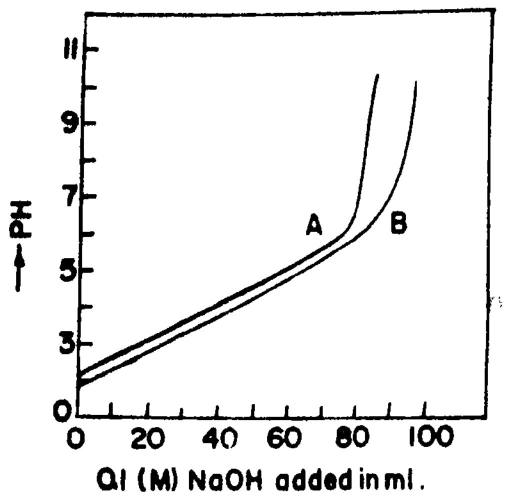


Fig. 2. *p*H titration of 100 ml of a solution containing 0.0025 g moles of citric acid and 0.01 g moles of KCl (Curve A) and that of the same volume of another solution containing the same quantity of the above constituents and 0.0005 g moles of dimethyl tin dichloride (Curve B) against 0.1 *N* sodium hydroxide

The values of n are calculated from the experiment (I) by equation (2-i) as in the case of cadmium citrate complex and are recorded in the Table 1. The value of n is found to be greater than 2, 3 and 4 above *p*H 3.6, 4.8 and 6.5 respectively. Below *p*H 3.6, a neutral complex is formed with the liberation of 2 protons. The formation of the complex C is complete at *p*H 3.6. The values of C are calculated below this *p*H by the equation (2) assuming the n values to be 2. The values of K were calculated and tabulated in the Table 1. The mean value of K is found to be 2.29×10^{-3}.

At and above *p*H 3.6, n is greater than 2 indicating the dissociation of the neutral complex C to C_1^- and H^+ according to the equation (3).

$$C \rightleftharpoons C_1^- + H^+ \quad \cdots \quad (3)$$

$$K_1 = \frac{[C_1^-][H^+]}{[C]} \quad \cdots \quad (3\text{-i})$$

It can be shown as before that,

$$K_1 = \frac{(n-2)[H^+]}{(3-n)}$$

The values of K calculated by the above equation are recorded in the Table 1. The mean value of K is 6.31×10^{-5}.

In higher *p*H (above 4.8) the complex C_1^- dissociates to $C_2^=$ and H^+ according to the equation (4). The equilibrium constant is represented by the equation (4-i).

$$C_1^- \rightleftharpoons C_2^= + H^+ \quad (4)$$

$$K_2 = \frac{[C_2^=][H^+]}{[C_1^-]} \quad (4\text{-i})$$

Similarly it can be shown that

$$K_2 = \frac{(n-3)[H^+]}{(4-n)}$$

The values of K_2 are recorded in the Table 1 and the mean value is found to be 5.48×10^{-6}.

TABLE 1

pH	Δ[NaOH] $\times 10^3$	− Δ[Cit] $\times 10^4$	[M] $\times 10^3$	a/b	n	[C] $\times 10^3$	$[M^{++}]$ $\times 10^4$	$[H_2Cit]$ $\times 10^4$	K $\times 10^3$	$K_1 \times 10^5$	$K_2 \times 10^6$	$K_3 \times 10^9$
2.8	4.094	2.77	4.63	0.3588	1.2643	2.555	20.75	20.57	1.503			
3.0	4.397	3.0	4.565	0.4822	1.4769	2.993	15.72	14.18	1.343			
3.2	4.894	3.35	4.505	0.6197	1.7517	3.697	8.08	7.766	2.845			
3.4	4.804	3.28	4.465	0.7632	1.8952	4.089	3.76	4.31	3.99			
3.6	5.112	3.43	4.417	0.9078	2.1348	—	—	—	—	3.913		
3.8	4.808	3.26	4.378	1.052	2.229	—	—	—	—	4.707		
4.0	4.914	3.59	4.34	1.204	2.435	—	—	—	—	7.7		
4.2	4.807	3.28	4.291	1.362	2.586	—	—	—	—	8.932		
4.8	4.91	3.31	4.178	1.876	3.199	—	—	—	—	—	3.939	
5.0	4.67	3.16	1.151	2.049	3.330	—	—	—	—	—	4.925	
5.2	4.59	3.1	4.116	2.213	3.495	—	—	—	—	—	6.184	
5.4	4.5	3.05	4.088	2.374	3.493	—	—	—	—	—	3.871	
5.5	4.13	2.79	4.065	2.450	3.634	—	—	—	—	—	5.478	
5.8	4.07	2.75	4.033	2.654	3.843	—	—	—	—	—	8.509	
7.2	5.01	3.4	3.891	2.981	4.529	—	—	—	—	—	—	7.087
7.4	5.16	3.48	3.886	2.988	4.583	—	—	—	—	—	—	5.567
7.5	5.44	3.67	3.87	2.988	4.677	—	—	—	—	—	—	6.628
7.8	5.44	3.78	3.861	2.995	4.697	—	—	—	—	—	—	3.646
8.0	5.84	3.95	3.847	2.997	4.823	—	—	—	—	—	—	4.649
8.2	5.98	4.02	3.841	2.997	4.868	—	—	—	—	—	—	4.149

Above pH 6.5 the n values are greater than 4 indicating the formation of the complex C_3^{3-}.

$$C_3^{-} \rightleftharpoons C_3^{3-} + H^+ \quad \ldots (5)$$

$$K_3 = \frac{[C_3^{3-}][H^+]}{[C_3^{-}]} \quad \ldots (5\text{-i})$$

The equilibrium constant is calculated by the equation

$$K_3 = \frac{(n-4)[H^+]}{(5-n)} \quad \ldots (5\text{-ii})$$

The mean value of K_3 is 5.28×10^{-8} and recorded in the Table 1.

The nature of curves in the Figures 3 and 4 are very similar. In the Fig. 4, the ratio of the metal to ligand is 1 : 5 and hence the formation of the complex is complete. The pH attained by the solution containing dimethyl tin by the addition of 11 ml of 0.1N NaOH is reached in the blank solution without the metal by the addition of 1 ml of 0.1N NaOH solution. Hence 0.0011 g mole of NaOH is consumed by the complex formed from 0.0005 g mole of dimethyl tin dichloride. This indicates the liberation of two protons. The complex C_1^{-} can be assumed to be formed by the interaction of dimethyl tin and sodium citrate. Hence the liberation of two protons indicates the formation of C_3^{3-} complex. It has been observed in the experiment (I) and Table 1 that in the pH range of 6.5 to 8.2, both C_3^{-} and C_3^{3-} species exist. The same equilibria will hold good in the experiment (IV) (Fig. 4). In this case

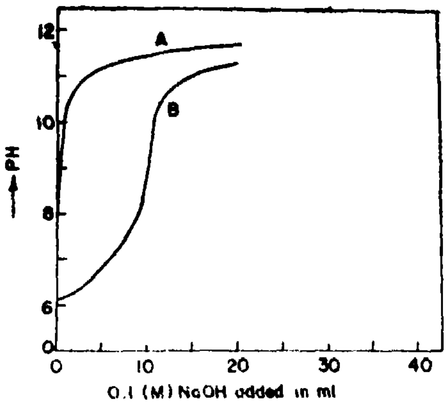


Fig. 4. pH titration of 100 ml of a solution containing 0.000625 g moles of sodium citrate and 0.01 g moles of KCl (Curve A) and that of another solution containing same quantity of the above constituents and 0.0005 g moles of dimethyl tin dichloride (Curve B) against 0.1N sodium hydroxide.

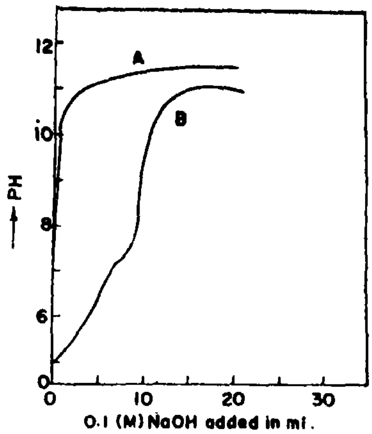


Fig. 3. pH titration of 100 ml of a solution containing 0.0025 g moles of sodium citrate and 0.01 g moles of KCl (Curve A) and that of another solution of same volume containing the same quantity of the above constituents and 0.0005 g moles of dimethyl tin dichloride (Curve B) against 0.1N sodium hydroxide.

$$[\text{Dimethyl tin}] = [C_3^{-}] + [C_3^{3-}]$$

$$\text{Free citrate} = [H_3Cit] + [H_2Cit^{-}] + [HCit^{=}] = X[HCit^{=}]$$

$$\text{where} \quad X = 1 + \frac{[H^+]^2}{k_1 . k_2} + \frac{[H^+]}{k_2} + \frac{k_3}{[H^+]}$$

$$[Cit] = [\text{Dimethyl tin}] + X[HCit^{=}] \quad \ldots (6)$$

It can be shown that acid liberated

$$= [C_3^{-}] + 2[C_3^{3-}]$$

TABLE 2—DETERMINATION OF K_3 VALUES FROM EXPERIMENT-II

pH	$[Cit]\times 10^3$	$[NaOH]\times 10^3$	$[M]\times 10^3$	X	$[HCit^{=}]\times 10^6$	Y	$[C_3^{-}]\times 10^4$	$[C_3^{3-}]\times 10^4$	$K_3\times 10^8$
7.1	23.58	5.315	4.718	41.792	451.4	1.00394	10.49	36.69	2.274
7.2	23.47	5.729	4.695	52.3515	358.6	1.00313	13.93	33.02	2.668
7.3	23.36	6.142	4.673	65.6512	284.5	1.0024	17.54	29.19	3.011
7.4	23.32	6.349	4.665	82.3709	226.4	1.0019	19.1	27.55	2.76
7.5	23.25	6.549	4.65	103.3007	180.1	1.0015	20.8	25.7	2.56
7.6	23.2	6.754	4.641	130.0006	142.8	1.0012	22.55	23.86	2.874
7.7	23.15	6.955	4.63	163.4004	113.3	1.0009	24.38	21.92	2.219
7.8	23.11	7.16	4.622	205.4003	89.97	1.0007	25.88	20.34	2.017
8.0	22.94	7.752	4.587	325.0	36.46	1.0004	32.21	13.66	2.358
8.4	22.78	8.343	4.557	814.7	22.37	1.0001	38.08	7.49	2.024
9.0	22.62	8.923	4.526	3241.0	5.582	1.00004	44.02	1.24	3.55
9.2	22.62	8.923	4.526	5136.0	3.552	1.00003	44.0	1.26	2.204

Acid neutralised $=[\mathrm{NaOH}]+[\mathrm{HCit}^-]+2[\mathrm{H_2Cit}^-]$

Hence $[\mathrm{C}_3^-]+2[\mathrm{C}_3^{2-}]=[\mathrm{NaOH}]+[\mathrm{H}^+]+\mathrm{Y}[\mathrm{HCit}^-]$ (7)

where $\mathrm{Y}=1+\frac{2[\mathrm{H}^+]}{k_3}$

or $[\mathrm{C}_3^{2-}]=[\mathrm{NaOH}]+[\mathrm{H}^+]+\mathrm{Y}[\mathrm{HCit}^-]-[\mathrm{Dimethyl\ tin}]$ ... (8)

$[\mathrm{H\,Cit}^-]$ has been calculated by equation (6).

The values of $[\mathrm{C}_3^{2-}]$ are obtained by equation (8) and $[\mathrm{C}_3^{2-}]$ has been calculated by subtracting $[\mathrm{C}_3^{2-}]$ from [Dimethyl tin].

The K_3 values calculated by equation (5-i) from this experiment are recorded in the Table 2. The mean values of K_3 is 2.5×10^{-8} which is exactly similar to that obtained in the experiment (I).

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 783-786

NMR and Magnetic Susceptibility Studies of Nitro-Ammine Cobalt(III) Complexes

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Manuscript received 2 January 1979, accepted 6 June 1979

A series of nitro-ammine cobalt(III) complexes have been reported. The ^{59}Co nuclear magnetic resonance (n m.r.), magnetic susceptibility and electronic spectra of these complexes were studied. The order of ligand field theory obtained from n.m.r. and residual paramagnetic susceptibility data are in fair agreement with optical data. The ^{59}Co nuclei in the said series of complexes are more shielded than the aquo, carbonato and oxalato series of cobalt(III)-ammine complexes. The deviation of the ^{59}Co chemical shifts and residual paramagnetism versus reciprocal of the energy of the first d-d electron transition is attributed to covalent bonding of ligands configurational interaction (*cis* and *trans*) and low symmetry crystal fields of the complexes.

IT has been well known that the trivalent cobalt forms a number of spin paired diamagnetic octahedral complexes. The ^{59}Co n.m.r. chemical shifts and magnetic susceptibility for Co(III) complexes have been reported by earlier workers[1-8]. Recently the residual paramagnetism of cobalt in the few series of Co(III)-ammine complexes was reported elsewhere[9-10]. Since nitro-ammine Co(III) complex series has not been studied so far, a systematic study, in conjunction with n.m.r. magnetic susceptibility and electronic spectra has been reported in this paper.

Materials and Methods :

Preparation of complexes : All the complexes of nitroammine Co(III) were prepared according to the modified methods described elsewhere[11] and then purified. The analytical data (Table 1) for the complexes were used for the identification and as a criterion for purity.

Physical measurements : The n.m.r. measurements were made on Varians wide line spectrometer V4200 at about 10,000 gauss. In this set up the homogeneity of the magnetic field over the sample volume and R.F. stability are good enough to give a resolution of better than 50 milligauss and therefore the shifts of the order of a gauss or more can be easily studied. The shift measurements were made in aqueous solution at room temperature (22±2°). The values of chemical shifts (σ%) observed for these complexes have been expressed :

$$[H_i - H_r/H_r] \times 100$$

where H_i is the resonance field for cobalt complex under study and H_r for the field of reference compound $K_3[Co(CN)_6]$ at constant frequency. The electronic spectra of the complexes were taken on a Hilger Uvispeck spectrophotometer, model H 700, using 1 cm matched quartz cells. The magnetic susceptibilities of the complexes were determined at room temperature by Gouy method, employing pure dried KCl and Hg $[Co(CNS)_4]$ as calibrants.

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Results and Discussion

The observed chemical shifts (σ) for the nitro-ammine Co(III) complexes are given in Table 1. The values are negative since the resonance occurs at a field lower than that for the reference $K_3[Co(CN)_6]$, and the shifts are quite large about 7,000 to 10,000 ppm relative to reference complex.

The residual paramagnetic contribution (σ para) which is the most dominant term in shielding in Co(III) complexes has been calculated for the complexes under investigation, [column (5), Table 1] using the relation given by Griffith and Orgel[12]. The data in column (4) can be compared with those in column (5) in which the observed values of relative chemical shifts have been converted to the absolute values by adding σ para for $K_3[Co(CN)_6]$ (−1.53)[5].

The results of magnetic susceptibility measurements are given in Table 1. The calculation and other details of these values are given elsewhere[9]. The diamagnetic correction $\Sigma\chi_D$ for the constituent atoms were calculated assuming Pascal's additivity rule for the complexes under study[9]. The choice of these diamagnetic correction values is arbitrary due to divergent reported data in the literature[14] and it is difficult to choose any one value as more reliable than the other.

The results indicate that the observed χ_M values for all the complexes are much smaller than $\Sigma\chi_D$ values. The difference between the two is obviously due to residual paramagnetism due to cobalt. In the n.m.r. method chemical shift depends on the

TABLE 1—ANALYSIS, CHEMICAL SHIFT, MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRAL DATA FOR NITRO-AMMINE Co(III) COMPLEXES

Complex	Found (%)	Cal (%)	Observed σ values	Observed absolute σ% values	Calculated σ para%	$10\chi_M$	$\Sigma\chi_D$	χ_p(obs)	χ_p(cal)	Orbital reduction factor k	Energy separation in cm^{-1} between $^1A_{1g} \rightarrow {}^1T_{1g}$
1	2	3	4	5	6	7	8	9	10	11	12
1. $[Co(NH_3)_6]Cl_3$	Co 22.32 NH_3 38.37	22.30 38.20	−0.810	−2.0340	−2.342	63.21	181.6	118.4	194.0	0.76	21050
2. $[Co(NH_3)_5NO_2]Cl_2$	Co 23.41 NH_3 32.68	22.60 32.70	−0.752	−2.282	−2.239	40.58	154.6	114.0	185.5	0.78	22030
3. $[Co(NH_3)_5ONO]Cl_2$	Co 22.29 NH_3 32.83	22.58 32.63	0.870	−2.400	−2.375	32.31	154.6	122.3	196.8	0.79	20750
4. $[Co(NH_3)_4(NO_2)_2]Cl$ *cis*	Co 22.92 NH_3 26.30	23.12 26.73	−0.715	−2.245	−2.204	86.83	127.6	100.8	182.6	0.74	22370
5. $[Co(NH_3)_4(NO_2)_2]Cl$ *trans*	Co 22.96 NH_3 26.42	23.12 26.73	−0.688	−2.238	−2.169	31.35	127.7	96.3	179.7	0.73	22720
6. $[Co(NH_3)_4(ONO)_2]Cl$ *cis*	Co 23.33 NH_3 20.25	23.12 26.73	−0.898	−2.428	−2.502	20.84	147.6	126.8	207.3	0.78	19760
7. $[Co(NH_3)_4H_2OONO'(NO_2)_2$ *cis*	Co 18.54 NH_3 21.32	18.75 21.62	−0.971	−2.501	−2.514	14.38	144.8	130.4	203.3	0.79	19610
8. $[Co(NH_3)_4H_2ONO_2](NO_3)_2$ *cis*	Co 18.21 NH_3 21.43	18.75 21.62	−0.830	−2.360	−2.336	30.50	144.8	114.3	193.6	0.77	21100
9. $[Co(NH_3)_4NO_2Cl]Cl$ *trans*	Co 24.48 NH_3 27.71	24.14 27.97	−0.818	−2.348	−2.357	18.78	137.5	118.8	195.4	0.78	20920
10. $[Co(NH_3)_3(NO_2)_3]$	Co 23.90 NH_3 20.63	23.80 20.73	−0.647	−2.177	−2.144	4.89	100.6	95.5	177.7	0.73	22990
11. $[Co(NH_3)_3(NO_2)_2Cl]$	Co 24.87 NH_3 21.03	24.82 21.52	−0.719	−2.249	−2.219	3.513	110.5	107.0	183.9	0.76	22220
12. $Na[Co(NH_3)_2(NO_2)_4]$	Co 19.79 NH_3 11.11	19.64 11.32	−0.622	−2.152	−2.070	41.51	103.7	92.2	171.6	0.73	23810
13. $Na_2[Co(NH_3)(NO_2)_5]$	Co 16.58 NH_3 4.66	16.74 4.82	−0.610	−2.140	−2.036	18.60	106.6	88.0	168.8	0.71	24210
14. $Na_3[Co(NO_2)_6]$	Co 14.25 N 20.68	14.59 20.80	−0.735	−2.285	−2.385	2.21	109.6	111.8	197.7	0.74	20660

Magnetic Susceptibility data are in the units of -1×10^{-6} cgs.

fact that in the octahedral complexes of Co(III), only one state, namely $^1T_{1g}$ of d^6 configuration of cobalt, can mix with the ground state $^1A_{1g}$ so that contribution of second order paramagnetism to the shielding parameters depends inversely on the energy separation between the two states. From this study one is inclined to believe that the main contribution to the shifts is the residual paramagnetism while the diamagnetic contribution has minor role in affecting the σ values.

It is seen that the replacement of ammonia ligand by nitro ion in these complexes results on decrease in σ values instead of increase in σ values as in case of aquo[3], carbonate[4] and oxalato[6] series of Co(III)-ammine complexes. Further σ decreases with an increase in the number of nitro groups in the complex $[Co(NH_3)_6]Cl_3$ which means that the shielding increases with substitution of the electronegative nitro group in the coordination sphere of Co(III) complex. The increase is in the order for nitro-ammine Co(III) complexes: hexammine<pentammine<tetrammine (*cis* and *trans*)<triammine<mono ammine<hexanitro (without ammonia ligand).

From the Table 1, it is seen that few mixed ligand and few nitritoammine Co(III) complexes behave differently from the rest of the complexes in this series because of oxygen and chlorine bonding towards cobalt along with nitrogen bonding in the complex moiety.

To compare the above order with the spectral data the absorption spectra of these complexes were studied in the visible region and a weak absorption due to d-d transition was found. The energy separation between the ground state $^1A_{1g}$ and excited state $^1T_{1g}$ of d^6 configuration was estimated from these bands (Table 1). The values show that the successive replacement of NH_3 ligand by nitro group increase the energy separation between the two states, further E values increases as successively as the number of nitro group in coordination sphere of complex increases. On the same line in magnetic susceptibility data residual paramagnetism value (χ_p) decreases regularly from hexammine to mono ammine (Table 1). Hexanitro cobaltate behaves differently from the rest of the complexes as far as n.m.r., magnetic and electronic spectral data are concerned. This may be due to mixture of nitro and nitrito ligands in the said complex.

The n.m.r., magnetic and electronic data can also be utilized to establish the relative ligand field strength of the ligands such as ONO^-, H_2O, NH_3

and NO_2^- in these complexes (Table 1). From these values, it is inferred that H_2O and ONO^- are weaker than NH_3 and NH_3 is still weaker compared to NO_2 ligand. The strength of these ligands increases in the order : $H_2O > ONO^- > NH_3 > NO_2^-$ in confirmity with spectro-chemical series.

From the Table 1, it is also observed that linkage isomers can be more easily distinguished (nitro and nitrito) by n.m.r. method than any other physical methods. The yellow and red varieties of these isomers are known in the literature for nitrite Co(III) complexes. There is chemical shift of 12-18 gauss (at 10 K. gauss) between these isomers. The nitrite-ammine complexes (including mixed ligand nitrite also) of Co(III) exhibit two signals. The intensity of one is more than the other. The weaker signal was due to nitrito complexes and it slowly disappears when the specimen gets old. Similarly this study can be used to distinguish configurational mixing (*cis* and *trans*) (Table 1).

The values of k (orbital reduction factor) are in the range of 0.70-0.80. For pure d orbitals k = 1 and for low spin complexes of transition series k will close to unity, (1-k) being the measure of the deviation of actual orbitals from being pure orbitals. These values clearly indicate that there is significant orbital overlap. It is also possible to calculate χ_p values from the relation of Griffith[13]. It is seen from the results that the calculated χ_p values are larger than the observed. Griffith and Orgel[12] estimated the probable error (20 per cent) in their theoretical calculations. In some of our complexes the disagreement between χ_p (obs) and χ_p (cal) and

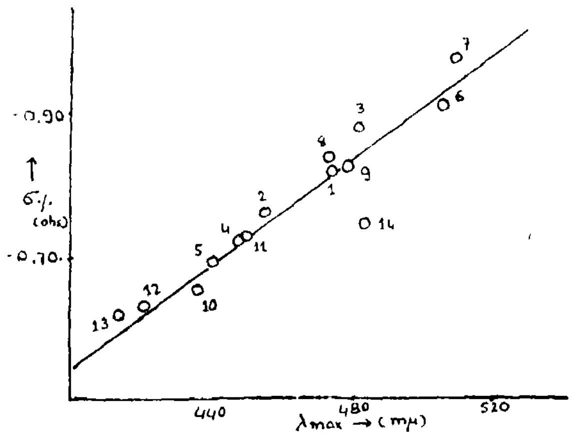


Fig. 1. The variation of chemical shift vs λ_{max}

even in n.m.r. results is outside the probable error. The theory[12] also predicts a linear relation between the ^{59}Co n.m.r. chemical shift versus the reciprocal of the energy of the first d-d electronic transition (λ_{max}) and residual paramagnetism (χ_p) versus λ_{max} (Figs. 1 and 2). It is seen from the figures that the correlation in case of n.m.r. results is fairly good but in magnetic susceptibility, it is not smooth.

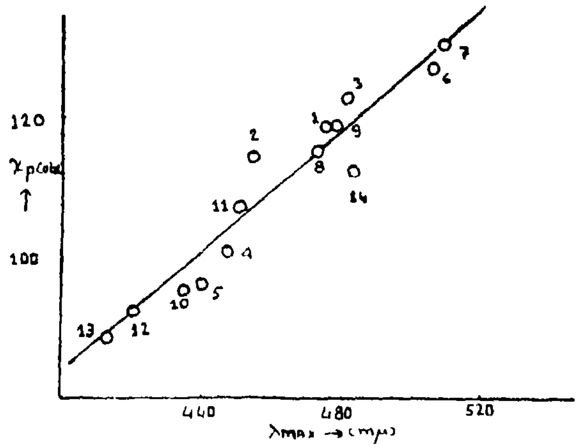


Fig. 2. The variation of χ_p(obs) vs λ_{max}

Eventhough such a linear relationship has been found to be approximately true[1,2] but the deviations from such a linear relationship now is also known[15,16]. We believe that main sources of deviations are covalent bonding of ligands in these complexes, uncertainties in the values of diamagnetic susceptibilities used for evaluating term, configurational interaction (*cis* and *trans*) and lastly the distortion in the octahedral ligand field from hexa ammine (O_h) to pentammine (C_{4v}), *trans* tetrammine (D_{4h}), *cis* (C_{2v}), triammine (C_{3v}) etc.

Acknowledgement

We are grateful to the authorities of Tata Institute of Fundamental Research, Bombay for running n.m.r. spectra. Thanks are due to late Prof. C. R. Kanekar for encouragement. We are also indebted to Shri V. R. Marathe for his help in experimental analysis and helpful discussion.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 787-791

Studies on the Colorimetric Determination of Silica in Rocks*, Part-I. An Investigation on the Ruggedness of the Differential Colorimetric Method of Determination

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Manuscript received 18 June 1979, revised 3 January 1980, accepted 21 May 1980

The differential technique of measurement of the absorbance of the less sensitive β-silico-12-molybdate complex was adopted for a precise colorimetric method for the determination of silica in rocks. In the development of the method a multivariant study was made to establish the robustness of the procedure. By the use of a permanent standard chromate solution as reference and two standard silica solutions of lower and higher concentrations to bracket the absorbance of the sample solution, a better precision of the method could be achieved. The method was employed successfully for the determination of silica in standard and other rocks containing appreciable amount of ferrous iron. Presence of phosphorus called for a small correction. The relative standard deviation of the method was around 0.4% in the concentration range of 40-70% SiO_2.

DETERMINATION of silica continues to be a problem in rock analysis. It is an enigma. The rapid instrumental methods, on the one hand, seem to be unacceptable to a large number of analysts when high precision and accuracy of the measurements are required, while, on the other hand, the laborious and time-consuming gravimetric method, by sheer high frequency of usage, achieves a dubious aura of popularity as could be seen from a recent study[1]. Of the rapid methods currently in use, the one by Shapiro and Brannock[2] is found to give results to a precision of about 1%. The method involving fusion of samples with lithium metaborate followed by determination of silica by atomic absorption measurement, as proposed by Suhr and Ingamells[3] and Van Loon and Parissis[4], was evaluated and recommended by Abbey. But in a subsequent publication[5] the same author concluded that the method was not really suitable at high concentrations of silica. The neo-classical approach consisting of gravimetry for the major portion of silica and spectrophotometry[6] or atomic absorptiometry[7] for the silica remaining in solution, seems to be the present trend towards improving the precision of silica determination. Use of organic flocculating agents has been recommended to hasten the coagulation and filtration of the bulk of the silica from acid solution.

Application of heteropoly silicomolybdate complex for the colorimetric determination of silica has received considerable attention. Optimisation of the experimental parameters to obtain a single species useful for accurate determination of silica has been discussed in detail in the earlier studies[8-15]. Chalmers and Sinclair[15] describe the use of acetone for intensifying and stabilising the coloured beta-molybdosilicate complex against fading and recommend the use of a permanent chromate standard prepared according to Swank and Mellon[16] for higher precision by differential colorimetry. The instrumental parameters needed for improving the precision have been evaluated by Abbey[5]. The main limitation in this method appears to be the rate of colour fading.

A detailed statistical evaluation of all the chemical parameters is carried out to evolve a rugged procedure suitable for the precise analysis of silica in rocks, and is described in this paper. Its accuracy has been evaluated by the analysis of a set of International rock standards of wide chemical composition.

Experimental

(a) Equipment :

1. Beckman Expandomatic SS-2 *p*H meter fitted with glass and calomel electrodes is used in the normal mode for *p*H measurement.

2. Beckman DU spectrophotometer and 1.00 cm cells are used for absorption measurements.

(b) Reagents :

All the reagents are of BDH AnalaR or E. Merck/S. Merck GR grade. All solutions are prepared with distilled water.

* Based on a paper presented at the symposium "Chemical Analysis of Geological Materials", Calcutta, 6—9 February, 1979.

1. 30% sodium hydroxide solution is prepared by dissolving 30 g sodium hydroxide pellets in about 50 ml water contained in a polyethylene beaker and diluting to 100 ml.

2. 6*N*-hydrochloric acid is prepared by diluting conc. hydrochloric acid of sp. gr. 1.18.

3. 2*N*-nitric acid is prepared by diluting conc. nitric acid of sp. gr. 1.42.

4. Potassium permanganate solution 0.05*N* approx.

5. Ammonium molybdate solution. A 10% (W/V) solution is prepared using $(NH_4)_6Mo_7O_{24}.4H_2O$. The mixture is warmed, if necessary, for complete solution, filtered and stored in a polyethylene bottle. The solution should be rejected on the appearance of turbidity.

6. $6N$-H_2SO_4 is prepared by diluting conc. H_2SO_4, sp. gr. 1.835.

7. 0.1*M* ammonium phosphate, $(NH_4)_2HPO_4$.

8. Standard reference stock solution. $3.22 \times 10^{-3} M$ potassium chromate in 0.1*M* ammonium phosphate buffer.

9. Working standard reference solution is prepared by diluting the chromate stock solution with 0.1*M* diammonium hydrogen phosphate solution. A set of such solutions, prepared with 8, 10, 12 ml, .. of the stock solution and made upto 100 ml, cover the silica contents in the range 40-70% in the samples. A solution prepared with 10 ml of the reference stock solution, has an absorbance equivalent to about 1.67 mg SiO_2 per 100 ml.

(c) Preparation of standard silica solution :

Take 5.0 ml of 30% NaOH solution (using a polythene pipette) in a nickel crucible of about 50 ml capacity, and evaporate to dryness on a hot plate. Weigh accurately by difference, about 100 mg of the standard silicate previously dried at 105°-110 and containing less than 70 mg SiO_2. Place the sample on the solid bed of sodium hydroxide in the crucible. U.S. Bureau of Standard Feldspar No. 99 containing 68.66% SiO_2 is used in this work. Place the crucible in a circular opening made in a thick asbestos plate exposing the bottom half of the crucible to the flame. Cover the crucible and fuse the sample for 10 min at a temp of 700° approx. Spread the melt on the inner sides of the crucible while cooling. Add about 15 ml of water and gently swirl the crucible for dissolution and detachment of the melt from its inner surface. Fill the crucible to half its volume with water and place it on a steam bath under cover for about half an hour. Alternatively, fill the crucible to about 40 ml with water and keep it overnight at room temperature. Transfer the contents quantitatively into a polythene beaker containing about 300 ml of water and 15.0 ml of 6*N*-hydrochloric acid or $6N$-H_2SO_4. Transfer the solution into a 500 ml volumetric flask and make up the volume with water. Mix and store the solution in a polythene bottle. The solution so prepared should have a *p*H value around 1.2.

(d) Preparation of sample and blank solutions :

Follow the steps used for the preparation of the silica standard solution to prepare sample solutions from the finely ground (-200 mesh) and dried samples (at 105°-110°). Prepare more than one process blank to ensure that the blank readings are low and reproducible. Centrifuge or filter the solution if it is turbid.

Recommended differential colorimetric procedure :

1. Take suitable aliquots of the sample (20 ml containing 2-3 mg SiO_2) and standard silica into 100 ml flasks.

2. Dilute the solutions to about 70 ml with water.

3. Add 3.0 ml of $2N$-HNO_3 and mix.

4. Add $0.05N$-$KMnO_4$ dropwise till a purple colour persists (two drops may be sufficient) and wash down the neck of the flask.

5. Add 10.0 ml of the molybdate solution slowly into one of the flasks, swirling during the addition, dilute to mark with water, and mix.

6. After 10 min., measure the absorbance of the yellow solution against the chromate solution at 400 nm.

7. Follow steps 5 and 6 in the case of other solutions.

Note :

(a) Measure the absorbances of a set of standard silica solutions of varied concentrations. Any sample examined shall be closely straddled by two standard solutions.

(b) Ensure that the interval between the time of colour development and measurement, is maintained the same for all the solutions.

(c) Measure any appreciable absorbance of the compensating sample solution (without the addition of molobdate) against blank for correcting the absorbance of the respective test solution. Also check the absorbances of the process blank solutions.

(d) The true value of SiO_2 in a silicate rock sample containing phosphate, can be obtained by applying a correction on the basis that the absorbance of 1 part P_2O_5 equals to that of 0.4 part SiO_2 (at 400 *nm*) which is obtained by actual experiment.

Calculation :

Obtain the silica content of the sample using the following expression,

$$\%\ SiO_2 = \left[L + (H - L) \times \frac{a_X - a_L}{a_H - a_L}\right] \times \frac{100}{W}$$

where L and H are the amounts of SiO_2 in the aliquots of the 'low standard' and the 'high standard', and W is that of the sample used for colour development and a_L, a_H and a_X are the corresponding absorbances.

Robustness of the Recommended Method :

The recommended procedure described above is evolved after carrying out a series of experiments designed to identify and control those factors to which the procedure could be vulnerable.

A schedule for the study of seven factors in eight combinations, as described by Youden[17] is adopted to establish the ruggedness of the procedure. The experimental design and the differences obtained in the values arising from deviations from predetermined conditions in one of the first set of experiments are given in Tables 1 and 2. It is clear that the time-dependent stability of the colour intensity, factor 'G' vs 'g', is poor. Hence the need for a closer control on this factor is indicated.

TABLE 1—EIGHT COMBINATIONS OF SEVEN FACTORS USED IN THE RUGGEDNESS TEST ; AN INITIAL STUDY

Combination No.	Vol. of 30% NaOH for fusion A/a (ml)	Time of fusion B/b (min)	Temp. of soln. (kept for 10 min) C/c (°C)	Normality of (15 ml)HCl for acidification D/d (N)	Volume of $3N-HNO_3$ E/e (ml)	Volume of 10% $MoO_4^=$ F/f (ml)	Time interval before colour measurement G/g (min)	Result $\%SiO_2$
1.	A	B	C	D	E	F	G	68.38
2.	A	B	c	D	e	f	g	72.19
3.	A	b	C	d	E	f	g	70 44
4.	A	b	c	d	e	F	G	64.77
5.	a	B	C	d	e	F	g	66.60
6.	a	B	c	d	E	f	G	64.06
7.	a	b	C	D	e	f	G	65.00
8.	a	b	c	D	E	F	g	69.14

A=7	B=15	C=30	D=7	E=3	F=12	G=15
a=5	b=10	c=20	d=5	e=2	f=10	g=10

Note : 1. A fixed volume of persulphate solution is added to each test solution.
2. See Ref. 17 for details of the schedule.

TABLE 2—RESULTS FROM THE RUGGEDNESS TEST LAID DOWN IN TABLE 1

Factor (F)	Alternate levels of F	Average result* of 4 combinations $\%SiO_2$	Difference (D)	D^2
Amount of alkali 30%	7.0 ml 5.0 ml	68.94 66.20	2.74	7.51
Time of fusion	15 min 10 min	67.80 67.34	0.46	0.21
Temp. of dissolution	30°C 20°C	67.60 67.79	0.19	0 04
HCl added (15 ml)	7*N* 5*N*	68 68 66.47	2.21	4.88
HHO_3 added (3*N*)	3.0 ml 2.0 ml	68.00 67.14	0.86	0.74
$MoO_4^=$ used (10%)	12 ml 10 ml	67.22 67.92	0.70	0.49
Colour stability	15 min 10 min	65.55 69.59	4.04	16.32

* e.g., the effect of alkali at the 1st level 'A' corresponds to the average of the results from combination numbers 1 to 4 in Table 1 ; similarly the effect of time of fusion at the 2nd level 'b' corresponds to the average of the results of combination numbers 3, 4, 7 and 8.

Another factor which needs control is the quantity of sodium hydroxide used for fusing the sample. This factor controls the *pH* of the solution which in turn influences the formation of the alpha or beta form of the heteropoly acid. In comparison it is seen that some other factors such as the time of fusion, factor B ; the temperature at which the sample solution is prepared, factor C ; and the quantity of the molybdate added, factor 'E' have smaller influence on the results. Hence control of their critical parameters as well as some other possible variables are included in further factorial studies which led to a final set of experiments (Table 3). The observed deviations are given in Table 4. Since the final differences are small, the precision of the measurements is computed and found to be about 0.4% in the determination of silica in rocks at a concentration level of 67%.

Results and Discussion

A prerequisite for the colorimetric determination of silica is that it should remain in solution in the

TABLE 3—EIGHT COMBINATIONS OF SEVEN FACTORS USED TO TEST THE RUGGEDNESS OF THE RECOMMENDED ANALYTICAL METHOD FOR THE DETERMINATION OF SILICA

Combination number	Volume of NaOH (30%, fusion for 10 min) A/a (ml)	Extraction of the melt B/b	Normality of HCl (15 ml for acidification) C/c (N)	Volume of HNO_3 (2N) D/d (ml)	Amount of 0.05N-$KMnO_4$ added in excess E/e (drops)	Volume of MoO_4^- (10%) F/f (ml)	Time interval before colour measurement G/g (min)	% SiO_2 found
1	4.5	C/W O.N.	5.5	2.8	1	9.5	10	67.32
2.	,,	,,	6.5	,,	2	10.5	12	67.52
3.	,,	H/W, ¼ hr	5.5	3.2	1	,,	,,	67.51
4.	,,	,,	6.5	,,	2	9.5	10	67.63
5.	5.5	C/W, O.N.	5.5	,,	,,	,,	12	67.33
6.	,,	,,	6.5	,,	1	10.5	10	67.12
7.	,,	H/W, ¼ hr	5.5	2.8	2	,,	,,	67.51
8.	,,	,,	6.5	,,	1	9.5	12	67.86
Final recommended condition	5.0	C/W, O.N.	6.0	3.0	1	10.0	10	67.50

C/W, O.N. = Extraction with cold water keeping overnight.
H/W, ¼ hr = Extraction with hot water keeping on steam bath for ¼ hour.

TABLE 4—RESULTS OBTAINED FROM THE RUGGEDNESS TEST AS LAID DOWN IN TABLE 3

Factor (F)	Alternate levels of F	Average results of 4 combinations % SiO_2	Difference (D)	D^2
Amount of alkali (30% NaOH)	4.5 ml 5.5 ml	67.49 67.45	0.04	0.0016
Condition of extraction	C/W, O.N. H/W, ¼ hr.	67.31 67.62	0.31	0.0961
HCl added to bulk soln. (15 ml)	5.5N 6.5N	67.41 67.78	0.37	0.1369
HNO_3 added to test soln. (3N)	2.8 ml 3.2 ml	67.50 67.40	0.10	0.010
Excess $KMnO_4$ (0.05N)	1 drop 2 drops	67.45 67.50	0.05	0.0025
Molybdate solution (10%)	9.5 ml 10.5 ml	67.51 67.41	0.10	0.010
Colour stability (time)	10 min 12 min	67.40 67.55	0.15	0.0225

$$S.D. = \sqrt{\frac{\Sigma D^2 \times 2}{7}} = 0.28$$

Coefficient of variation is 0.4% for a sample at the concn. level of 67% SiO_2.

reactive form as monosilicic acid[16]. The sample size, acidity, and the final volume are recommended to ensure this condition.

Addition of specified amounts of the reagents as described in this procedure, brings the final *p*H of the solution to the optimal range of 1.0-1.8[14], which is considered most favourable for the formation of beta-silicomolybdic acid. The molybdate concentration is maintained between 0.05*M* and 0.06*M*. The formation of alpha-acid under these conditions is not expected as it is a slow process and is accelerated by higher *p*H at elevated temperature[11].

Precision of the results improves as the absorbances of the standard and the sample approach each other, and hence the choice of two closely bracketing silica standards. It is, however, necessary to complete the absorbance measurement within 10-12 min to avoid colour fading. The rate of fading of the colour of the silicomolybdate complex during the next 30 min after the stipulated time of 10 min is found to be about 2%. The addition of permanganate ensures complete oxidation of ferrous to ferric state. The effects of interfering elements like As, Ge and V are neglected as their concentrations in the normal silicate rocks, are very low.

A number of standard rock samples with diverse chemical compositions have been analysed for their silica contents to check the accuracy and reproducibility of the method. The results are given in Table 5. By adherence to the recommended procedure the relative standard deviation of the method is found to be within 0.4% in the concentration range 40-70% SiO_2.

TABLE 5—ANALYSIS OF STANDARD ROCK SAMPLES

	Standard sample	Recommended value % SiO_2	Range of values found by present method % SiO_2
1.	PCC-1	41.90[19]	(i) 41.76 (ii) 41.84
2.	AGV-1	59.00[19]	(i) 58.92 (ii) 59.26
3.	GSP-1	67.38[19]	(i) 67.38 (ii) 67.37
4.	MRG-1	39.24[1]	(i) 39.23 (ii) 39.14
5.	Trachyte (TKT)	67.66[a] 67.10[b]	(i) 67.38 (ii) 67.57

(a) By Shapiro and Brannock method.
(b) By Gravimetric method.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 792-796

Separation of Lanthanons by Paper Electrophoretic Method and Determination of Their Mobilities by the Same Technique

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Manuscript received 28 November 1978, revised 14 February 1980, accepted 13 May 1980

Separations of Ce(IV) from Y(III), La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) in potassium oxalate or oxalic acid; La(III) from Y(III), Dy(III); Ce(IV) from La(III), Pr(III), Nd(III), Sm(III); and Sm(III) from Y(III), Dy(III) in sodium acetate-sodium citrate electrolytes were successfully achieved by paper electrophoresis at low voltage.

MOBILITIES of tripositive lanthanides were calculated from their ionophoretic speeds on paper after correcting for electro-osmotic and tortuosity effects at different concentrations of hydrochloric acid as supporting electrolyte. It was found that mobilities decrease, with the increase in atomic number of the lanthanides, with the increase in strength of the supporting electrolyte, and with the decrease in ionic radii of the tripositive lanthanons. It is due to the hydrolysis of the tripositive lanthanides which increases with increasing atomic number and contraction in radii and also due to fall in conductance with increasing concentration of the supporting electrolyte.

Lanthanons and their homologues have similar mobilities and chemical properties, so their separations by electromigration are quite difficult. However, some lanthanons were separated by many workers[1-28] by using organic acid or its salt as background electrolyte by high voltage or continuous electrophoretic technique. The authors attempted to separate lanthanons by paper electrophoresis at low voltage using different electrolytes. Only the separations of (a) Ce from Y, La, Pr, Nd, Sm, Gd and Dy in 0.1N potassium oxalate (pH 7.5) or 0.1N oxalic acid in 3 hrs' run; (b) (i) La from Y and Dy, (ii) Ce from La, Pr, Nd and Sm and (iii) Sm from Y and Dy in mixed electrolyte sodium acetate-sodium citrate were successfully achieved.

Experimental

Wieland and Fischer[29] type horizontal electrophoretic set was used in the experiment for the separations of lanthanides. Paper strips (2 × 34 cm) from Whatman No. 1 were used as supporting medium. Potential gradient of 3 volts/cm in 0.1N potassium oxalate, 6.1 volts/cm in 0.1N oxalic acid, 2.1 volts/cm in mixed electrolytes (0.1N sodium acetate and 0.1N sodium citrate), and 4.5 volts/cm in mixed electrolytes (0.2M lactic acid and 0.2M citric acid) were maintained in the separation of lanthanons.

Determination of Mobilities of Lanthanons :

The mobilities of tripositive lanthanides have been calculated from their ionophoretic speeds on paper after correcting for electro-osmotic and tortuosity effects at different concentrations of hydrochloric acid as supporting electrolyte.

The important factors influencing the speed of ions are : (i) electro-osmotic effect owing to the movement of the charge particles, and (ii) tortuosity factor or 'added migration path-length' owing to the winding nature of the path created by the fibrous structure of the filter paper.

Correction for electro-osmosis :

As an electro-osmotic indicator, the large polysaccharide molecules or smaller sugar molecules can be used on account of their very low mobilities in free electrophoresis at low pH.

If d_I be the distance that a migrant travels on a paper strip, measured from the origin, and d_G, the distance that an uncharged glucose molecule travels in the same direction at low pH, the net distance that the migrating ion travels is $(d_I - d_G)$. The mobility U_I is expressed by :

$$U_I = \frac{d_I - d_G}{Xt} \quad \cdots \quad (I)$$

where 'X' is the field strength and 't' is the time In the same way, the speed of electro-osmotic flow may be expressed by :

$$U_{el} = \frac{d_G}{Xt} \quad \cdots \quad (II)$$

From equations (I) and (II)

$$\frac{d_G}{d_I - d_G} = \frac{U_{el}}{U_I}$$

The ratio $\frac{U_{el}}{U_I}$ is constant regardless of distance, time or field strength, and thus $\frac{d_G}{d_I - d_G}$ or $\frac{d_I}{d_G}$ is constant.

Correction for "added migration path-length" :

The formulae employed for the determination of free solution mobilities, viz.,

$$U = \frac{dL}{dV} \text{ and } U = \frac{D_q K}{it}$$

(where, V is the voltage, L, the length of the channel, d, the distance of migration, t, the time, q, the cross sectional area, i, the current and K, the specific conductance in mho/cm) are not applicable to liquids in a highly porous supporting medium, namely, paper. It may be shown that the expression for field strength, $\frac{V}{L}$ and $\frac{i}{qK}$ are not equal, as L does not represent the true distance of voltage drop through the paper, i.e., L the length, is not the length of the channel inside the network of paper fibres, nor d the actual distance the ions move, but rather a length L' and a distance d' have to be considered.

Since, $L' = L\left(\frac{L'}{L}\right)$ (1)

therefore $d' = d\left(\frac{L'}{L}\right)$ ... (2)

and it can be shown that

$$d = \frac{ut\,V}{L}\left(\frac{L}{L'}\right)^2 \quad .. \quad (3)$$

Also, since in free solution the particle migrates a distance

$$d = \frac{ut\,i}{qK} \quad ... \quad (4)$$

in paper this becomes $d' = \frac{ut\,i}{q_a K}$ (5)

where q_a is the cross-sectional area of the paper.

We have also from the previous equations (2) and (5)

$$d = \frac{ut\,i}{q_a K}\left(\frac{L}{L'}\right) \quad ... \quad (6)$$

that is, equations (3) and (6) differ from the free electrophoresis by the term $\left(\frac{L}{L'}\right)$, the correction factor for calculating the mobility on paper. It was possible to determine the correction factor using $L' = Rq_aK$, where R is the resistance of the paper strip.

For the determinations of the mobilities of tripositive lanthanides, four measurements were made under each set of experimental conditions. These included measurements of ionographic mobility and R_D, a modified R_f as in classical chromatography of the migrant and of the electro-osmotic indicator. The general expression

$$U = \frac{U_E}{R_D^M} = \frac{U_{el}}{R_D^{el}}$$

were U_E denotes the ionographic mobility of the migrant and U_{el} that of the indicator and R_D^M and R_D^{el}, denote the R_D values of the migrant and the indicator, respectively, have been utilised for the determination of free solution mobilities of some inorganic ions. The negative sign is used in the right-hand side of this equation if the migrant is positively charged, if it is charged negatively, the positive sign is used.

Preparation of materials :

0.01 molar solutions of Rare-Earth nitrate were prepared. The background electrolytes, 0,05*M*, 0.1*M* and 0.2*M* hydrochloric acid (A.R.), were prepared. The reagents employed for detecting the ionic species were also prepared, viz., saturated alcoholic sodium salt of Alizarin S for Rare-Earths (colour of the band – red-violet, brown or red) ; 10 vol of H_2O_2 for Ce(IV) (colour of the band – brown) ; 2*N* H_2SO_4 and aniline oxalate (100 ml of 0.1*N* oxalic acid & 0.9 ml aniline) for glucose (colour of the band – brown).

Apparatus :

Micropipettes (1 ml capacity, graduated up to 10^{-3} ml) were used to spot a small volume of the substance under investigation on chromatographic paper. The horizontal paper electrophoretic set, which utilises the horizontal paper strips in the electrolyte saturated condition, was used with Whatman chromatographic paper no. 1.

The paper strips used are previously saturated with the relevant solvent in desiccator. There are one outlet and one inlet at the base of the chamber (Fig. 1) through which a steady stream of nitrogen gas, saturated with relevant solvent vapour, can be passed. The latter is then made gas-tight, to all intents and purposes, by placing a cover and then closing the junctions of the cover and the top of the base by means of cellophane adhesive tape. This arrangement allows the temperature of the chamber to be maintained almost constant between 29° and 31°, thus reducing evaporation of the solvent from the strips to a minimum.

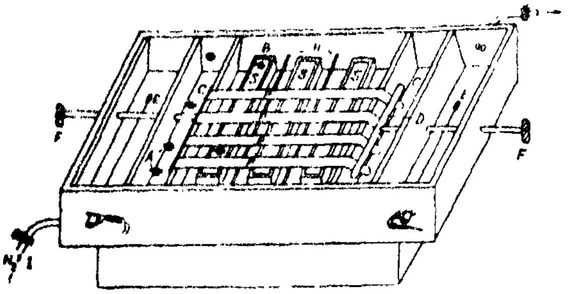


Fig. 1. A = Stoppered hole for solvent addition. B = Stoppered hole for application of substance. C = Electrolyte chamber, D = Fixer plate for paper strip, E = Electrodes, F = Turning screw for fixer plate, H = Hanger for paper strips, P = Paper strips, S = Solvent vessel and I = Inlet for nitrogen.

Procedure :

To start the experiment, two strips were simultaneously used. They were moistured carefully with the electrolyte adjusted to definite *p*H from the ends avoiding any excess of electrolyte. They were then pressed gently between two dry filter paper sheets in order to make them, as far as possible, uniformly wet. The strips were then placed in the rack so that they were kept horizontally tant by pressing them gently between and by two glass slabs on each end inside each of the electrolyte vessels. In order that each strips might offer the same resistance towards current flow, which could be observed from the equal length of each strip exposed above the solvent level, the mid-point line of each strip was just made to touch the pointed end of a narrow plastic stick on which it rested. Electrolyte was then poured to the same level in each electrode vessel in order to avoid hydrodynamic flow of fluid in the paper, which is independent of electrical potential. The cover was then placed in position, the chamber made gas-tight and a direct current at a potential of 200 volts was applied for five minutes in order to drain out any excess of solvent. The flow of current was then carefully spotted to the marked midpoint of each of the strips. The cover was then quickly replaced and again a direct current at a potential of 200 volts was applied for half an hour. The strip was then dried and sprayed with reagent specific for the particular rare-earth ion and again dried. The distance of migration of the ion was measured as usual.

In the determination of the R_D values of the ions, two strips (50 cm × 3 cm) were simultaneously used. Each strip was marked by a pencil at two places, the first at a distance of 10 cm and the second at 13 cm from one end of the strip. The first mark was used to indicate the position of application of the substance under investigation and second for the solvent front. These measurements were used in each experiment in which R_D values were determined. The marked strips were then fixed in position to the adjustable paper-holding glass slabs, pulled horizontally tant placed inside the chamber, below which solvent was placed in three small vessels for saturation of the strips with solvent vapour. After saturating the strips with solvent vapour, a definite volume = 300 ml of the solvent was poured in the vessel kept just below the ends of the strips through a funnel placed in the hole on the cover. The hole was closed by a soft rubber cork as soon as the solvent was poured. The solvent rose up gradually and when the solvent front reached the second mark, the same amount of the salt as used in the ionophoresis experiments, was applied on the first mark through the cork-up hole on the cover just above the second mark. The run was allowed to proceed for half an hour when appreciable movement of the solvent front took place. The strips were then taken out by removing the cover, dried and developed by the reagent specific for the particular rare-earth ion under investigation. The distance traversed by a particular ion from the first mark and that by the solvent front from the second mark were noted, and thus the R_D value for the substance was calculated.

The distance of migration, together with the R_D values were utilised for calculation of free solution mobilities.

A series of similar experiments were performed with the ions of the Rare-Earths with HCl as

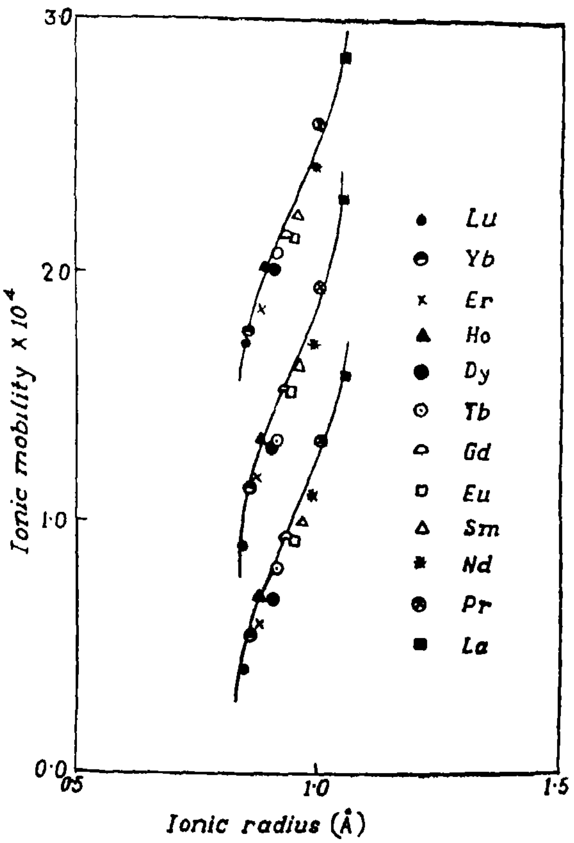


Fig. 2.

electrolyte at *p*H values : 1.3, 1.0 and 0.69. The distances of migration of the different ions and those of glucose used as the electro-osmotic indicator in hydrochloric acid, adjusted to the above *p*H values, have been measured and shown in Table 1. The R_D values of these ions together with those of glycose also in hydrochloric acid at the above mentioned *p*H values are given in Table 2. The observed mobilities and computed free solution mobilities (in terms of cm^2/volt-sec) of the ions under investigation are given in Tables 3A and 3B, and represented graphically in Fig. 2 as function of ionic radii.

TABLE 1—POTENTIAL GRADIENT = 4.5 Volts/cm. TIME = 90 MINUTES, TEMPERATURE = 29.31°C, ELECTROLYTIC MEDIUM = HCl OF DIFFERENT CONCENTRATIONS

Migrant	Distance of migration in cm.		
	0.05*M* HCl (*p*H = 1.3)	0.1*M* HCl (*p*H = 1)	0.2*M* HCl (*p*H = 0.69)
Glucose	0.7	0.7	0.7
La^{3+}	3.0	2.5	2.0
Ce^{4+}	1.5	1.3	1.0
Pr^{3+}	2.8	2.3	1.8
Nd^{3+}	2.6	2.1	1.6
Sm^{3+}	2.6	2.0	1.6
Eu^{3+}	2.5	2.0	1.5
Gd^{3+}	2.4	2.0	1.5
Tb^{3+}	2.4	1.8	1.4
Dy^{3+}	2.3	1.8	1.3
Ho^{3+}	2.4	1.9	1.3
Er^{3+}	2.2	1.7	1.2
Yb^{3+}	2.2	1.7	1.2
Lu^{3+}	2.0	1.5	1.0

TABLE 2—DETERMINATION OF 'R_D' VALUES IN HYDROCHLORIC ACID OF DIFFERENT CONCENTRATIONS

Substance	0.05*M* HCl (*p*H = 1.3)	0.1*M* HCl (*p*H = 1)	0.2*M* HCl (*p*H = 0.69)
Glucose	0.90	0.92	0.95
La^{3+}	0.97	0.95	0.98
Ce^{4+}	0.98	0.98	0.99
Pr^{3+}	0.97	0.98	0.99
Nd^{3+}	0.95	0.97	0.98
Sm^{3+}	1.00	0.96	1.00
Eu^{3+}	0.99	0.99	1.00
Gd^{3+}	0.95	0.99	1.00
Tb^{3+}	0.97	0.98	0.99
Dy^{3+}	0.95	0.99	0.99
Ho^{3+}	0.99	0.99	0.99
Er^{3+}	0.96	0.98	0.98
Yb^{3+}	0.99	1.00	1.00
Lu^{3+}	0.99	1.00	1.00

TABLE 3A—VARIATION OF MOBILITY OF IONS WITH CHANGE OF CONCENTRATION OF ELECTROLYTE

Migrant	0.05*M* HCl Mobility × 10^4 cm^2/volt-sec. (Observed)	0.1*M* HCl Mobility × 10^4 cm^2/volt-sec. (Observed)	0.2*M* HCl Mobility × 10^4 cm^2/volt-sec. (Observed)
Glucose	0.8642	0.8642	0.8642
La^{3+}	3.703	3.086	2.469
Ce^{4+}	1.852	1.603	1.234
Pr^{3+}	3.452	2.839	2.222
Nd^{3+}	3.210	2.592	1.975
Sm^{3+}	3.210	2.469	1.975
Eu^{3+}	3.086	2.469	1.852
Gd^{3+}	2.963	2.469	1.852
Tb^{3+}	2.963	2.222	1.728
Dy^{3+}	2.839	2.222	1.604
Ho^{3+}	2.963	2.346	1.604
Er^{3+}	2.716	2.098	1.481
Yb^{3+}	2.716	2.098	1.481
Lu^{3+}	2.469	1.852	1.234

TABLE 3B

Migrant	Atomic number	Ionic radii M^{3+} (°A)	0.05*M* HCl Mobility × 10^4 (cm^2/volt-sec) (Compound)	0.1*M* HCl Mobility × 10^4 (cm^2/volt-sec) (Compound)	0.2*M* HCl Mobility × 10^4 (cm^2/volt-sec) (Compound)
La^{3+}	57	1.061	2.86	2.31	1.61
Ce^{4+}	58	—	0.93	0.70	0.94
Pr^{3+}	59	1.010	2.60	1.96	1.34
Nd^{3+}	60	0.995	2.42	1.78	1.11
Sm^{3+}	62	0.964	2.25	1.68	1.06
Eu^{3+}	63	0.950	2.16	1.55	0.94
Gd^{3+}	64	0.938	2.16	1.55	0.94
Tb^{3+}	65	0.923	2.09	1.34	0.84
Dy^{3+}	66	0.908	2.03	1.31	0.71
Ho^{3+}	67	0.894	2.03	1.33	0.71
Er^{3+}	68	0.881	1.87	1.20	0.60
Yb^{3+}	70	0.858	1.78	1.16	0.57
Lu^{3+}	71	0.848	1.53	0.91	0.32

Discussion

It is seen from Tables 3A and 3B and Fig. 1 that mobilities decrease, with the increase in atomic number, with the increase in strength of the electrolyte, and, with the decrease in ionic radii. The reason for the low mobility of the tripositive lanthanide ions at the lower strengths of hydrochloric acid is due to their hydrolysis.

The M^{3+} aquo ions are hydrolysed[30] according to $M(H_2O)_n{}^{3+} + H_2O \rightleftharpoons M(H_2O)_{n-1}(OH)^{2+} + H_3O^+$ and the tendency to hydrolysis increases with increasing atomic number as would be expected from contraction in radii.

The smallest ion, Lu^{3+}, should have the largest mobility, but it actually has the lowest in the series. This discrepancy can be explained as :—the ions are attached in solution to a number of water molecules, and these "hydrated ions" migrate as a whole under the *influence of the applied potential gradient.* If the lanthanum ion is more highly hydrated than praseodymium, and so on through the series, the size of the ion-hydrated complex *may* decrease in going from lanthanum to lulecium. In view of the high polarizing power of a small ion, it is probable that the attraction between the ions and the molecular dipoles of water will decrease steadily with increasing atomic weight, as required to account for the observed *ionic mobilities.*

So, due to hydrolysis the sizes of the ions increase with increasing atomic number, and as a result the mobilities decrease sharply, Ce^{4+} ion has much lower mobilities, because the very highly charged Ce^{4+} ion has a pronounced tendency to

hydrate[30] and the hydrate ion, $Ce(H_2O)_n^{4+}$, is a strong acid.

Again the mobility of an ion decreases with increasing electrolyte concentration due mainly to the falling off in conductance with increasing concentration. In more strong electrolyte, the electrostatic attraction between positive and negative ion persists, i.e., there may be a definite pairing of ions or a continual interchange of partners between ion-pairs. The consequence of this is that although ionization may be complete, dissociation will be incomplete except in very dilute electrolyte. The quantity of electricity that can pass through an electrolyte, and hence its conductance, depends on the product of the number of ions, the charge carried by each ion, and the velocity with which the ions move. Since the total charge is a constant in each case, the conductance of an electrolyte can only depend on the speeds of the ions. So, as the conductance falls with increasing concentration of the electrolyte, the mobility of an ion falls.

Acknowledgement

Authors' thanks are due to Dr. M. M. Lahiri of Belur R. K. M. and Dr. S. K. Mukherjee, Ex-Vice-Chancellor, Calcutta University for their constructive suggestions and to the U.G.C. for the award of research grant.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 797-799

Kinetics and Mechanism of Ag^+ Catalysed Oxidation of Alcohols by Peroxodisulphate Ion in Aqueous Medium

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Manuscript received 24 August 1979, revised 17 March 1980, accepted 13 May 1980

The kinetics of Ag^+ catalysed oxidation of 3-butane-2-ol, 2-methyl-3-butane-2-ol, *n*-butyl alcohol and allyl alcohol by peroxodisulphate ion in aqueous medium revealed that although these reactions are first order in $S_2O_8^{2-}$, first order in Ag^+ and zero order in substrate in any particular kinetic run, the pseudo first order rate constant is dependent on the concentration of $S_2O_8^{2-}$ and substrate taken. The stoichiometry in case of 3-butane-2-ol is 1 : 1 and varies in case of 2-methyl-3-butane-2-ol. Allyl acetate inhibits the rate appreciably indicating that the reaction involves free radicals or radical ions. The salt effect is negative and of primary exponential type. The product of oxidation in each case is the corresponding aldehyde. On the basis of kinetic behaviour reported and the products characterised, a general radical mechanism for these reactions has been proposed and the corresponding rate law has been derived.

OXIDATION of alcohols by peroxodisulphate ion is an interesting reaction. Although a large amount of work has been done to decide the mechanism of Ag^+ catalysed oxidation of alcohols by peroxodisulphate ion, it is still undecided and differing kinetic behaviours have been reported. Thus Edwards *et al*[1], found a 1.5 and 0.5 order in CH_3OH and C_2H_5OH, while Stehlik and Fiala[2] observed half order inhibition by alcohol for these reactions. On the other hand, Khulbe and Srivastava[3] reported zero order in alcohol and first order in $S_2O_8^{2-}$ for the Ag^+ catalysed oxidation of 2-propanol. A detailed kinetic study of Ag^+ catalysed oxidation of 3-butane-2-ol and 2-methyl-3-butane-2-ol has been undertaken in order to arrive at a general mechanism for these oxidation reactions. The effect of temperature on the oxidation of *n*-butyl alcohol and allyl alcohol has also been carried out to test the isokinetic relationship. The results of these studies are presented and discussed in this paper.

Experimental

Methods and Materials :

3-Butane-2-ol (E. Merck), 2-methyl-3-butane-2-ol (L. R. Aldrich) and allyl alcohol ; *n*-butyl alcohol (B.D.H. AnalaR) were used after distillation. Purity of the compounds was also checked by their boiling point. All the inorganic chemicals used were of AnalaR grade.

The reaction was carried out in aqueous medium and its progress was followed by estimating the unreacted $K_2S_2O_8$ iodometrically by the method of Szabo, Gsyani and Galiba[18], as modified by Khulbe and Srivastava[19].

The IR spectra were recorded on Beckman IR-20, Infrared Spectrophotometer using KBr disc.

Results and Discussion

Kinetic behaviour :

Kinetic studies at constant ionic strength and at different concentrations of $K_2S_2O_8$ and substrates show that the reaction in each case is first order in oxidant and zero order in substrate. However, the first order specific rate is dependent on the concentration of $K_2S_2O_8$ and the alcohol (Table 1). The specific rate is linearly related to Ag^+ (Table 2). In both the cases, the reaction exhibits negative salt effect of the exponential type (Table 3). The reaction shows appreciable inhibition of rate by allyl acetate (Table 4). The thermodynamic parameters for the oxidation of the four alcohols under study are reported in Table 5. A plot of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ for different alcohols is linear, indicating the applicability of isokinetic relationship and the value of β calculated therefrom is 321.2°K.

The mole ratio of substrate to oxidant comes out to be 1 : 1 in case of 3-butane-2-ol while it varies in case of 2-methyl-3-butane-2-ol.

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TABLE 1—EFFECT OF VARYING REACTANT CONCENTRATIONS ON THE SPECIFIC REACTION RATE

$[AgNO_3] = 1.0 \times 10^{-3} M$ $\mu = 0.631 M$. Temp. = 308K

$[K_2S_2O_8] \times 10^2 M$	[Substrate] $\times 10^2 M$	Specific rate $sec^{-1} \times 10^4$
	3-butane-2-ol	
1.0	1.0	0.19
2.0	1.0	0.23
3.0	1.0	0.25
4.0	1 0	0.26
1.0	2.0	0.31
1.0	3 0	0.31
1.0	4.0	0.33
1.0	5.0	0.34
	2-methyl-3-butane-2-ol	
1.0	1.0	0.040
2.0	1.0	0.053
3.0	1.0	0.060
4.0	1 0	0.067
1.0	2.0	0.057
1.0	3.0	0.070
1.0	4.0	0.070

TABLE 2—EFFECT OF $[AgNO_3]$ ON SPECIFIC REACTION RATE

Temp = 308K

$[K_2S_2O_8] = 0.01 M$ $[K_2SO_4] = 0.2 M$

[3-butane-2-ol] or [2-methyl-3-butane-2-ol] = 0.01 M

$AgNO_3 \times 10^3 M$	$k \times 10^4 sec^{-1}$ 3-butane-2-ol	$k \times 10^4 sec^{-1}$ 2-methyl-3-butane-2-ol
1.0	0.19	0.38
2.0	0.38	0.70
2.5	0.47	0.83
3.0	0.55	1.00
3.5	0.65	—

TABLE 3—EFFECT OF IONIC STRENGTH ON SPECIFIC RATE

Temp. = 308K

$[K_2S_2O_8] = 0.01 M$ $[AgNO_3] = 0.001 M$

[3-butane-2-ol] or [2-methyl-3-butane-2-ol] = 0.01 M

Ionic strength μ	$k \times 10^4 sec^{-1}$ 3-butane-2 ol	$k \times 10^4 sec^{-1}$ 2-methyl-3-butane-2-ol
0.031	6.2	1.0
0.061	5.3	0.98
0.091	4.6	0.85
0.121	4.0	0.78
0.151	3.7	0.75
0.181	3.4	0.71

TABLE 4—EFFECT OF ALLYL ACETATE ON THE SPECIFIC REACTION RATE

Temp. = 308K

$[K_2S_2O_8] = 0.01 M$ $[AgNO_3] = 0.001 M$

[3-butane-2-ol] or [2-methyl-3-butane-2-ol] = 0.01 M

[Allyl acetate]	$k \times 10^4 sec^{-1}$ for 3-butane-2-ol	$k \times 10^4 sec^{-1}$ 2-methyl-3-butane-2-ol
0.000	6.30	1.03
0.002	5.80	0.770
0.010	4.30	0.770
0.100	0.800	0.050

TABLE 5—THERMODYNAMIC PARAMETERS

Substrate	Temp. coeff.	Ea. K. cals mole^{-1}	A $\times$ sec^{-1}	$\Delta G^{\neq}$ K. cal mole^{-1}	$-\Delta S^{\neq}$ E.U.	$\Delta H^{\neq}$ K. cal mole^{-1}
3-butane-2-ol	1.08	12.7	1.99×10^4	24.9	41.0	12.0
2-methyl-3-butane-2-ol	2.07	14.6	9.30×10^4	26.0	37 9	14.0
n-butyl alcohol	2.25	16.3	9.43×10^6	24.6	28.7	15.7
Allyl alcohol	2.40	17.9	4.15×10^7	25.2	25.8	16.9

Analysis of the Product :

The product of reaction in case of 3-butane-2-ol and 2-methyl-3-butane-2-ol was isolated from the reaction mixture by distillation under reduced pressure. The distillate in each case gave +ve test for aldehydic group with Schiff's reagent. To characterise the different aldehydes formed, the 2,4-DNP derivatives of the products were prepared and recrystallised with alcohol, and checked for purity by TLC, and these were characterised by elemental analysis, m.p. IR and by co-tlc to be ?-butane-2-one and methyl-vinyl-ketone respectively.

Mechanism :

Taking into consideration the previous proposed mechanism for this redox system and on the basis of the kinetic results obtained and the products of oxidation characterised, the following general mechanism is proposed for the oxidation of these alcohols by $S_2O_8^{2-}$:

$$\text{(i)} \quad Ag^+ + S_2O_8^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AgS_2O_8^- \; ; \; K = \frac{k_1}{k_{-1}}$$

$$\text{(ii)} \quad AgS_2O_8^- \xrightarrow{k_2} Ag^{2+} + SO_4^{\cdot-} + SO_4^{2-}$$

$$\text{(iii)} \quad RCH_2OH + SO_4^{\cdot-} \xrightarrow{k_3} RCH_2\dot{O} + HSO_4^-$$

$$\text{(iv)} \quad RCH_2OH + Ag^{2+} \xrightarrow{k_4} RCH_2\dot{O} + Ag^+ + H^+$$

$$\text{(v)} \quad R\dot{C}HOH + S_2O_8^{2-} \xrightarrow{k_5} RCHO + HSO_4 + SO_4^{\cdot-}$$

$$\text{(vi)} \quad R\dot{C}HOH + SO_4^{\cdot-} \xrightarrow{k_6} RCHO + HSO_4^-$$

Applying steady state treatment to the different reactive intermediates viz. Ag^{2+}, $SO_4^{\cdot-}$ and $R\dot{C}HOH$, the following rate law is obtained for the consumption of peroxodisulphate ion with time :

$$\frac{-d}{dt}[S_2O_8^{2-}] = k_2K\,[Ag^+][S_2O_8^{2-}] + \left(\frac{Kk_2k_3k_5}{k_6}\right)^{\frac{1}{2}}[ROH]^{\frac{1}{2}}[Ag^+]^{\frac{1}{2}}[S_2O_8^{2-}] \quad \ldots (1)$$

Since $k_6 >> K$ or k_2 or k_3 or k_5, the second term of equation (1) will be very very small, which is kinetically indistinguishable and hence can be neglected. Thus the rate of peroxodisulphate consumption can be approximated to

$$\frac{-d}{dt}[S_2O_8^{2-}] = k_2K[Ag^+][S_2O_8^{2-}]$$

However, the possibility of utilisation of $SO_4^{\cdot}$, formed in the process (ii), in oxidising Ag^+ in preference to RCH_2OH according to the following reaction cannot be ruled out

$$\text{(iiia)} \quad Ag^+ + SO_4^{\cdot} \xrightarrow{k_3'} Ag^{2+} + SO_4^{2-}$$

If process (iiia) occurs in place of process (iii), the rate law for the disappearance of $S_2O_8^{2-}$ works out to be

$$\frac{-d}{dt}\left[S_2O_8^{2-}\right] = \left[k_2K + \left(\frac{k_3Kk_2k_4}{k_5}\right)\right]^{\frac{1}{2}} [Ag^+][S_2O_8^{2-}] \quad \ldots (2)$$

Thus, both the rate laws derived satisfy all the kinetic features observed in the oxidation of alcohols studied. However, the dependence of the rate on the concentration of $S_2O_8^{2-}$ can be attributed to the effect of trace impurities present[4] even in the recrystallised samples of $K_2S_2O_8$.

Justification for the proposed mechanism :

Formation of $AgS_2O_8^-$ complex in the first step by a reversible process is in accordance with the view of Bekier and Kijowski[5], and Beilerian and Chaltykyan[6]. Large negative value of entropy of activation suggests that the first reversible step is a fast one while the second stage, the dissociation of $AgS_2O_8^-$ into three ions is a slow process. The existence of Ag^{2+} and $SO_4^{\cdot}$ in such redox systems has already been reported earlier by a number of workers[7-10]. $SO_4^{\cdot}$ has been shown to abstract hydrogen from the substrate in preference to $\dot{O}H$ as also suggested earlier by Anbar and Neta[11] and Hayon and Simic[12]. Greater tendency of direct oxidation by $SO_4^{\cdot}$ by one electron transfer compared to that by $\dot{O}H$ has already been shown by a number of workers[8-10] and recently has been confirmed by Steenken *et al*[13]. Our assumption that Ag^{2+} and $SO_4^{\cdot}$ are the chief reactive species is in agreement with the observation of Subbaraman and Santappa[14], and of Higginson and Marshall[15]. The absence of participation of $\dot{O}H$ in such a redox system has already been confirmed by Kumar[16], in his study of oxidation of diols by peroxodisulphate ion. In the fifth and sixth steps $R\dot{C}HOH$ has been used for further reaction instead of $RCH_2\dot{O}$, the formation of which is justified by the observation of Gilbert *et al*[17] in their ESR studies wherein they have found that $Pr\dot{O}$ undergoes a fast unimolecular isomerisation into $Et\dot{C}HOH$ (k value of the order of 10^7 sec^{-1}).

$$Pr\dot{O} \rightleftharpoons \dot{C}HOHEt$$

Further, free radical nature of the reaction has also been confirmed by us by the observance of appreciable inhibitory effect on the reaction by allyl acetate.

Acknowledgement

One of us (V. K. G.) is thankful to the Council of Scientific and Industrial Research, New Delhi for the award of Senior Research Fellowship.

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J. Indian Chem. Soc.,
Vol LVII, August 1980, pp. 800-803

Kinetics of Oxidation of Primary Alcohols by Acid Bromate

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Manuscript received 17 November 1979, revised 15 April 1980, accepted 12 June 1980

The kinetics of oxidation of primary alcohols by acid bromate has been studied in acetic acid-water medium in presence of sulphuric acid. Order with respect to oxidant was one and fractional with respect to substrate. The order of reacting alcohols is not regular and does not show correlation with Taft plot. Decomposition constants for the alcohol-bromate complexes were calculated and the plot of log k_d versus Taft σ^* values gave a linear plot with a slope of −0.70 indicating the formation of a transition state with small positive charge on α-carbon atom.

OXIDATION of several aliphatic, aromatic, primary and secondary alcohols and also alicyclic alcohols have been studied in detail by using different oxidants like Ce(IV)[1-4], Cr(VI)[5,6] and Br_2[7]. Oxidation of secondary alcohols by pure bromate was studied by Venkatasubramanian[8] *et al*, where they used mercuric acetate for complexing the product Br^- ion. Though bromate is a powerful oxidising agent in acid medium, it was used as a source of bromine in presence of Br^- ion. In the studies of bromate oxidation, the product Br^- ion formed in the reaction mixture reacts with Br(V) to generate bromine which on accumulation oxidises the substrate along with bromate ion. Hence to eliminate the bromine oxidation which is much faster than the oxidation by bromate ion, the product bromide ion, should be suitably complexed as soon as it is formed. This was achieved by using mercuric acetate.

In continuation of our earlier work[9] on the oxidation of phenols by bromate, we are communicating in this report the results of bromate oxidation of several primary alcohols, at various temperatures in the range 30-60° and in various amounts of acetic acid as solvent.

Experimental

Potassium bromate, (AnalaR, BDH) mercuric acetate (SM) samples were used as such. All the alcohols used were distilled collecting the required fractions. Acetic acid was purified by distillation. The oxidation of alcohols was studied in acid medium in 40% acetic acid and in the presence of mercuric acetate and sulphuric acid in the temperature range 30-60°. The experimental details are given in our earlier paper[9]. Mercuric acetate did not interfere in the oxidation reaction. The mercuric acetate was used as complexing agent to remove Br^- ions as $HgBr_4^{2-}$ as soon as they are formed. All the alcohols were oxidised to their corresponding aldehydes which were identified by the melting points of their 2, 4-D.N.P. derivatives.

Results and Discussion

The order with respect to the oxidant was found to be unity which is evident from the plots of log (a-x) versus time. Experiments were done with different initial concentrations of bromate and the pseudo-first order rate constants were independent of the initial concentration of bromate. A break in the first order plot was observed in the absence of mercuric acetate at the low concentration of sulphuric acid (0.05*M*) indicating slow bromate oxidation followed by fast bromine oxidation (Fig. 1). In presence of mercuric acetate the break disappeared and a linear plot was obtained. The rate constant

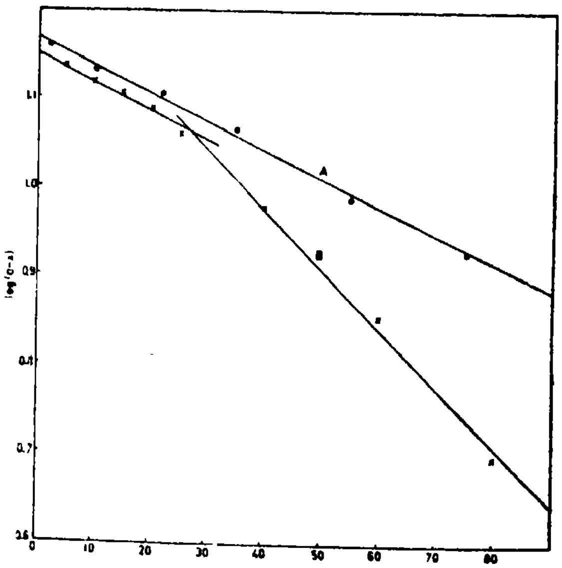


Fig. 1. Plots of log (a-x) versus time
$[BrO_3^-]=5\times10^{-3}M$, [Methanol]$=5\times10^{-2}M$, $[H_2SO_4]=0.05M$
Acetic acid = 40%, temperature = 45°C
(A) In the presence of Mercuric acetate.
(B) In the absence of Mercuric acetate.

obtained here was equal to the rate constant obtained from the first part of the plot prior to the break. We have conducted the oxidation of alcohols by bromate at 0.5*M* H_2SO_4 and 40% (v/v) acetic acid, without mercuric acetate. Here we never observed the break in the first order plot, though we observed the yellow colour due to bromine. The liberated bromine does not oxidise the substrate under these conditions whereas at 0.05*M* H_2SO_4 and 40% acetic acid the oxidation by bromine was evident. This indicates that the oxidation by bromine is suppressed at higher acid concentrations. When the experiment was repeated with mercuric acetate, same rate constant was obtained but no yellow colour due to free bromine was developed. The suppression of bromine oxidation at higher concentration of acid and at higher percentage of acetic acid was also observed in the oxidation of benzaldehydes[10] by bromine and also in the oxidation of hydroxy acids[11] by bromine, the rate of oxidation decreased on increasing sulphuric acid concentration and percentage of acetic acid.

The rate of oxidation of alcohols by bromate increases on increasing the concentration of sulphuric acid (Table 1). Plots of log k_{obs} versus log $[H_2SO_4]$ gave linear graph, the gradients of which were different for different alcohols, the values being in the range 1.3 to 1.9, thus showing that the dependence on $[H^+]$ is not simple.

TABLE 1—EFFECT OF SULPHURIC ACID ON THE RATE OF REACTION

$[\text{Substrate}]=5\times10^{-2}M$; $[BrO_3^-]=5\times10^{-3}M$; Acetic acid = 40% , [Mercuric acetate] = 0.01*M* , temp. = 30°C

Conc. of H_2SO_4	0.20	0.40	0.60	0.80	1.00
	$k\times10^3$ litres mol^{-1} sec^{-1}				
Substrate					
Methanol	4.01	6.98	13.92	23.28	29.52
Ethanol	0.95	2.56	4.65	6.61	8.84
n-Propanol	1.47	3.31	7.89	11.39	15.78
n-Butanol	0.80	1.97	3.73	7.33	11.39
iso-butanol	1.28	2.92	6.10	9.64	14.40
n-Pentanol	1.67	3.16	7.31	9.84	16.99
iso-pentanol	1.22	3.20	6.03	7.89	12.53
n-Hexanol	1.08	3.65	6.94	13.01	21.93
n-Heptanol	1.36	3.45	6.99	9.43	13.35
Benzyl alcohol	0.90	2.33	4.58	7.89	12.82
2-Phenyl ethyl alcohol	1.03	2.78	4.66	7.12	11.39
2-Cl-Ethanol	0.41	0.97	2.13	3.41	6.40

The reaction was studied at different concentrations of substrate. The slopes of log k_{obs} versus log (alcohols) were not strictly unity. The data also yielded linear plots of $1/k_{obs}$ versus 1/[ROH] with definite intercept, for all the alcohols studied, suggesting a rate expression of the type.

$$\frac{-d[Br(V)]}{dt}=\frac{k_d\,K[ROH][Br(V)]}{1+K[ROH]}$$

where K is the equilibrium constant for the formation of alcohol – Br(V) complex, and k_d is the decomposition constant of the alcohol – Br(V) complex. From the plots of $1/k_{obs}$ versus 1/[ROH] the decomposition constants were calculated.

The reactions were studied with different percentages (v/v) of acetic acid, and linear plots were obtained on plotting log k_{obs} versus 1/D with a positive slope indicating the reaction to be of ion-dipole. The positive ion should be the protonated bromate ion. According to Amis[12] equation, the distance of closest approach (r) of the reactants were calculated from the slopes, assuming the ion to be unipositive ion, for all the alcohols. The r values obtained were in the rangs of 0.5 to 1.0Å.

The oxidation was studied in the temperature range 30 to 60° and the thermodynamic parameters were calculated (Table 2). The more negative $\Delta S^{\neq}$ values indicate the rigid activated complex formation.

TABLE 2—THERMODYNAMIC PARAMETERS

$[H_2SO_4]=0.05M$; temp. = 45°C ; Acetic acid = 40% ; [Mercuric acetate] = 0.01*M*.

Substrate	$k_{obs}\times10^3$ ($lm^{-1}s^{-1}$)	$\Delta E^{\neq}$ K. Joules mol^{-1}	$\Delta H^{\neq}$ K. Joules mol^{-1}	$\Delta S^{\neq}$ Joules mol^{-1} $degree^{-1}$
Methanol	3.84	76.62	73.98	−59.00
Ethanol	0.66	69.67	67.03	−95.00
n-Propanol	1.07	56.11	53.47	−134.00
n-Butanol	0.92	63.85	61.21	—
iso-butanol	1.28	63.22	59.28	—
n-Pentanol	1.03	63.85	61.21	—
iso-pentanol	0.95	63.85	61.21	—
n-Hexanol	1.24	53.26	50.62	—
n-Heptanol	1.17	52.34	49.70	—
Benzyl alcohol	0.63	57.49	54.85	—
2-Phenyl ethyl alcohol	1.07	60.34	57.70	—
2-Cl-ethanol	0.31	81.31	78.67	−65.00

Basing on the experimental facts the possible mechanism was proposed (Scheme 1).

$$BrO_3^-+2H^+ \overset{K_1}{\rightleftharpoons} H_2^+BrO_3$$

$$RCH_2OH+H_2\overset{+}{Br}O_3 \overset{K_2}{\rightleftharpoons} R-CH_2-O-\overset{+}{Br}O_2H+H_2O$$

$$R-CH_2-O-\overset{+}{Br}O_2H \xrightarrow[\text{slow}]{k_3} R-CHO+H_2^+BrO_2$$

$$R-CH_2OH+H_2^+BrO_2 \longrightarrow R-CHO+H_2^+BrO+H_2O$$

$$R-CH_2OH+H_2^+BrO \longrightarrow RCHO+Br^-+2H^++H_2O$$

Scheme 1

From this mechanism the rate expression was derived in terms of total bromate concentration.

The rate expression obtained was,

$$\frac{-d[BrO_3^-]}{dt}=\frac{K_1K_2k_3[BrO_3^-]_T[H^+]^2[ROH]}{1+K_1[H^+]^2+K_1K_2[ROH][H^+]^2}$$

which explains the observed experimental facts. The first order rate constant can be given as :

$$k_{obs}=\frac{K_1K_2k_3[H^+]^2[ROH]}{1+K_1[H^+]^2+K_1K_2[ROH][H^+]^2}$$

When $1/k_{obs}$ is plotted against $1/[ROH]$ a straight line will be obtained with an intercept.

Intercept $1/k_3$

$$\text{slope}=\frac{1}{K_2k_3}+\frac{1}{K_1K_2k_3[H^+]^2}$$

Thus slope is dependent on $[H^+]$, and a plot of the slopes versus $1/[H^+]^2$ will give a straight line with an intercept $=\frac{1}{K_2k_3}$ and slope $=\frac{1}{K_1K_2k_3}$. From this intercept, slope data K_1, K_2 and k_3 can be calculated.

The effect of substrate at different $[H^+]$ was studied for the oxidation of ethanol (Table 3), 2-Cl-ethanol and *n*-butanol, and K_1, K_2 and k_3 were calculated. The K_1 value was found to be (0.2 l^2m^{-2}) for all the three substrates. Using this K_1 value (0.2 l^2m^{-2}) K_2 and k_3 values were calculated for other alcohols.

TABLE 3—EFFECT OF [ETHANOL] ON k_{obs} AT DIFFERENT $[H_2SO_4]$ IN BROMATE ETHANOL REACTION

$[BrO_3^-]=5\times10^{-3}M$; Acetic acid = 40% ; [Mercuric acetate] = 0.01M, temp. = 30°

$[C_2H_5OH]/M$	$k\times10^3$ min^{-1} at $[H_2SO_4]/M$ 0.4	0.6	0.8	1.0
5.0×10^{-2}	7.69	11.60	15.29	20.60
7.5×10^{-2}	13.90	19.60	24.39	32.26
1.0×10^{-1}	19.80	27.03	33.33	43.48
1.5×10^{-1}	26.53	34.48	41.67	52.63

The data obtained for the oxidation of different alcohols shows that there is no correlation between the rate and structure of the alcohols. There is no regular order of reactivity for the alcohols. This type of deviation was also observed in the oxidation of alcohols by Br_2[7] and Ce(IV)[8].

The equilibrium constant data for the bromate-alcohol complex formation shows that there is no correlation between the equilibrium constant and the polar nature of the alcohols.

The decomposition constants (k_3) were calculated from intercept of $1/k$ versus $1/[ROH]$ plot ; and the log k_3 was plotted against σ^* for methanol, ethanol, *n*-propanol, *n*-butanol, iso-butanol and 2-phenyl ethanol, a straight line with a slope of -0.70 (ρ^*) was obtained (Fig. 2). The ρ^* value suggests formation of a transition state, with a small carbonium

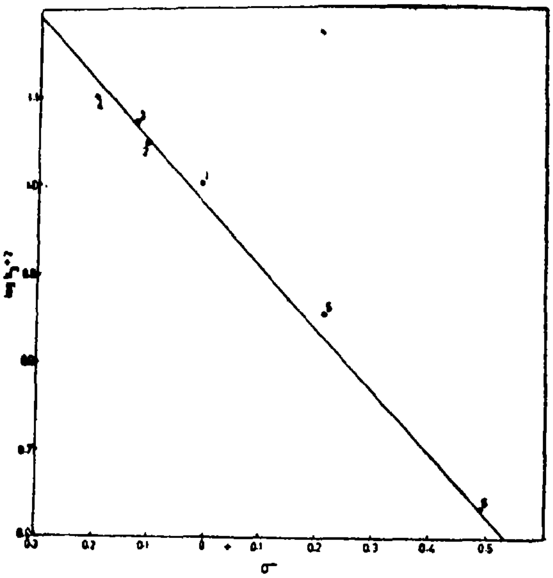


Fig. 2. Plot of log k_3 versus σ^* for primary alcohols.
(1) Ethanol (2) *n*-Propanol (3) *n*-Butanol (4) *Iso*-butanol (5) 2-Phenyl ethanol (6) Methanol.

ion character. Deviation was observed for the other alcohols with higher number of carbon atoms. The very high k_3 value for benzyl alcohol can be attributed to the resonance stabilisation of the charge on α-carbon atom which is directly attached to the ring.

Acknowledgement

One of the authors (Vijayalakshmi) wishes to thank C.S.I.R., (New Delhi) for award of J.R.F. and S.R.F.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 804-806

Studies on Azido Complexes of Cobalt—Part 2

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Manuscript received 15 May 1979, revised 26 December 1979, accepted 12 June 1980

The effects of solvents (water, DMSO, glycerol-water) on the u.v. absorption spectra of a few azido complexes of Co(III) have been studied. It has been observed that the absorption peaks are dependent on the composition of the solvent medium.

THE effect of solvents on charge transfer spectra of metal complexes, apart from their own intrinsic interest, have received attention as they throw light on the photochemically active precursors upon irradiation in the charge transfer region.

While a lot of data is available for acidopentamine complexes of the type $Co(III)L_5X^-$, complexes of the type $Co(III)L_4(X^-)_2$ and $Co(III)L_3(X^-)_3$, which are capable of forming *cis* and *trans* isomers, have received little attention. The object of the present investigation is to study the effects of the medium (water, glycerol solution and dimethyl sulphoxide) on the charge transfer spectra of *cis* and *trans* azido complexes of Co(III).

Experimental

The compounds have been prepared by standard methods and their spectra recorded in Beckman spectrophotometer Model DU. The blank in each case consists of a solution having the same medium composition as that of the complex solution. The spectra of *cis* and *trans* $[Co(NH_3)_4(N_3)_2]N_3$ were taken in an NaOAc/HOAc and phthalate buffer solution of *p*H 4 respectively in order to prevent hydrolysis. Except for slight changes in the value of the molar absorbance, peak positions in the visible and u. v. regions, remain unaltered in the *p*H range 3-5. Since $[Co(NH_3)_5Cl]Cl_2$ is sparingly soluble in DMSO and $[Co(bipy)_2(N_3)_2]ClO_4 \cdot 2H_2O$ is sparingly soluble in water, absorption maxima for these two compounds were obtained by plotting absorbance of nearly saturated solutions of these compounds in DMSO and water respectively.

There is some controversy about *cis* $[CO(NH_3)_3(N_3)_3]$. The method of preparation[1] for both *cis* and *trans* triazido complex is by warming aqueous solutions of either *cis* or *trans* $[Co(NH_3)_4(N_3)_2]N_3$ with sodium azide and ammonium sulphate at 60° with subsequent cooling of the reaction mixture. It was pointed out later[2] that *trans* $[Co(NH_3)_3(N_3)_3]$ is the exclusive product, whether one starts with *cis* or *trans* bisazido complex. It has been observed, however, that on cooling the reaction mixture containing the *cis* bisazido complex, various fractions of crystals are obtained. The last crop of crystals, obtained on prolonged cooling of the mother liquor in ice, on analysis, conforms to a triazido complex, with the following absorption bands in DMSO: visible, (550 n.m., 18180 cm^{-1}, $\epsilon_M = 212$) and u.v., (315 n.m., 31750 cm^{-1}, $\epsilon_M = 20850$). For the *trans* compound literature data[2] for the visible band in DMSO is 16990 cm^{-1}. Like the *trans* triazido complex, it is also insoluble in water and dissolves only in DMSO.

Results and Discussion

For all compounds a blue shift is observed in going from a solvent of lower dielectric constant, DMSO to one with a higher dielectric constant, water. A specific interaction between solute and solvent causes the shifts and the shifts are not related to the overall dielectric constant of the medium.

From peak position of the CTTM (charge transfer to metal) bands as given in Table 1, shifts as small as 340 cm^{-1}, as is observed for $[Co(NH_3)_5N_3]Cl_2$, may appear to be trivially small but it is clear from Fig. 1, (absorption spectra of $[Co(NH_3)_5N_3]Cl_2$ in different solvents) that the band in DMSO as a whole undergoes a distinct red shift with respect to water.

For *cis* and *trans* bisazido pairs, the blue shift is more pronounced for the *cis* than for the *trans* (Figs. 2 and 3).

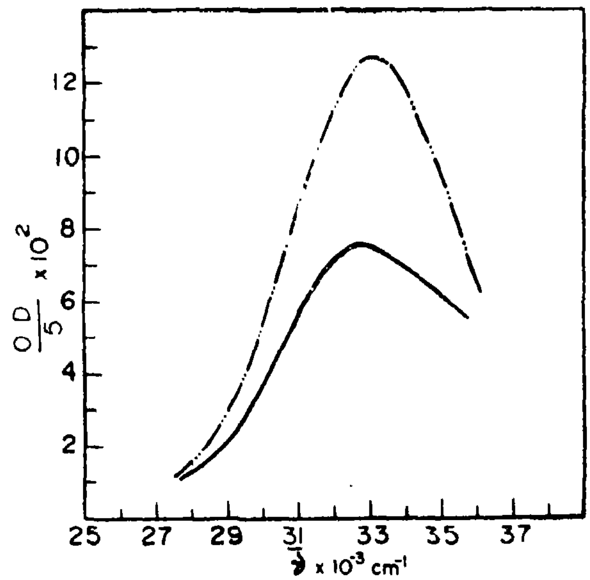
In conventional charge transfer complexes of the donor acceptor type a red shift of the charge transfer band is observed with increasing dielectric constant of the medium[3]. This is attributed to a progressively greater stabilisation of the excited state with the increasing polarity of the solvent medium.

In contrast to this behaviour, for all the complexes studied here, a blue shift is observed with increase in solvent polarity. This behaviour is in

TABLE 1

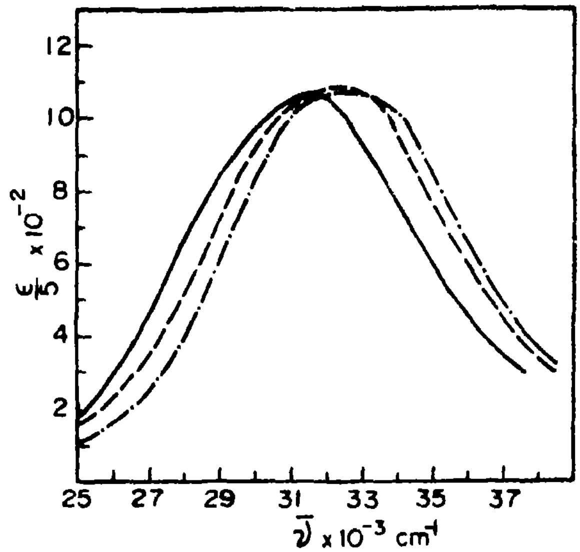
Complex	λ_{max}(nm),	$\bar{\nu}_{max}$(cm^{-1})	$\Delta\bar{\nu}_{max}$*(cm^{-1})	Solvent Conditions
$[Co(NH_3)_5N_3]Cl_2$	303,	33000		Water
	305,	32790	210	DMSO
	308,	32470		NaOAc/HOAc buffer pH 4
cis$[Co(NH_3)_4(N_3)_2]N_3$	309,	32360	110	90% glycerol in buffer
	317,	31550	920	DMSO
	340,	29410		Phthalate buffer pH 4
trans$[Co(NH_3)_4(N_3)_2]N_3$	341,	29330	80	90% glycerol in buffer
	346,	28900	510	DMSO
cis$[Co(NH_3)_3(N_3)_3]$	306,	32680		DMSO + H_2O (10% DMSO)
	315,	31750	930	(a) DMSO & (b) DMSO + Dioxane (1 : 1)
	305,	32790		(a) water & (b) 72% glycerol
cis$[Co(en)_2(N_3)_2]ClO_4$	307,	32570		90% glycerol
	310,	32260	530	DMSO
	340,	29410		Water
trans$[Co(en)_2(N_3)_2]ClO_4$	341,	29330		(a) 50% glycerol & (b) 90% glycerol
	344,	29070	340	DMSO
trans$[Co(en)_2N_3Cl]ClO_4$	321,	31150		(a) water (b) 50% glycerol (c) 90% glycerol (d) 50% (by wt.) of sucrose
	332,	30120	1030	DMSO
	302,	33110		Water
trans$[Co(dipy)_2(N_3)_2]ClO_4.2H_2O$	307,	32570	210	DMSO

* Red shift with respect to water.



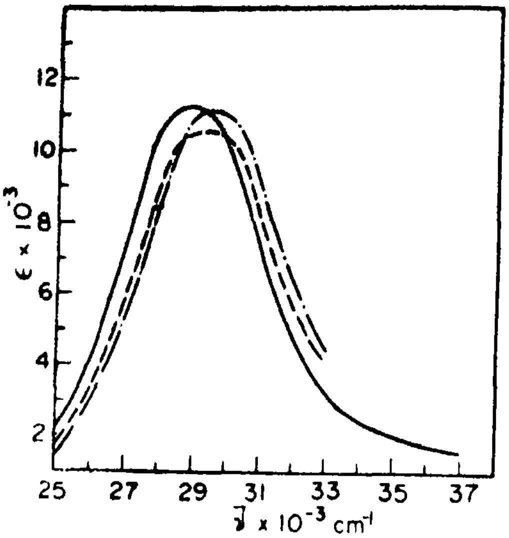
Absorption spectra of $[Co(NH_3)_5(N_3)]Cl_2$ in various media. DMSO(——), water (—·—·—)

Fig. 1



Absorption spectra of Cis $[Co(NH_3)_4(N_3)_2]N_3$ in various media: DMSO(——), 90% glycerol (– – –), Sodiumacetate-acetic acid buffer, pH-4, (—·—·—).

Fig. 2



Absorption spectra of trans $[Co(NH_3)_4(N_3)_2]N_3$ in various media : DMSO (——), 90% glycerol (- - - -), Potassium hydrogen phtholate buffer, pH-4 (—·—).

Fig. 3

conformity with the known behaviour[4] of compounds with an asymmetry in charge distribution and in which the transfer of charge is from ligand to metal (CTTM). During this transfer of charge the dipole moment of the excited state is reduced. The ground state, due to its higher dipole moment, is stabilised to a greater extent than the excited state.

Trans $[Co(en)_2N_3Cl]ClO_4$ and $[Co(NH_3)_5N_3]Cl_2$ belong to point group C_{4v}. Both *cis* bisazido and *trans* triazido complexes belong to C_{2v}. The symmetry of *cis* triazido[8] is C_{3v}, while that of *trans* bisazido is D_{4h}. Hence the above explanation cannot be used for the *trans* bisazido complexes, which cannot have a dipole moment due to the presence of a centre of inversion. It should be remarked that the azide ion is a linear polyatomic molecule, and if present in an eclipsed conformation, about the tetragonal axis, can bring about slight asymmetry in charge distribution in *trans* bisazido complexes.

Absorption maxima of all these compounds, in solutions with a low concentration of glycerol (50-70% by volume) and solutions containing 50% by weight of cane sugar, correspond to that in water. Even by using highly concentrated glycerol solution (90% by volume), there is little or no change in spectral peaks with respect to water. But a distinct red shift is observed in DMSO with respect to water although the dielectric constant of a 90% by volume aqueous solution of glycerol[5] and that of DMSO[6] are nearly equal (≃46). It is clear that dielectric constant, a bulk property of the medium, is not responsible for the shift. This is further corroborated by the observation that in mixed solvents such as DMSO+water & DMSO+dioxane, containing varying amounts of DMSO and dioxane, the peak positions do not undergo any intermediate shifts, but correspond entirely to that of the more polar solvent.

In both aqueous and non-aqueous media, the complex is exclusively in a solvent cage of the more polar component and remains unaffected by an increase in concentration of the less polar component.

In a few cases (*cis* and *trans* bisazido pairs), very high concentrations of glycerol is able to effect, although to a very small extent, the solvent cage of water molecules, and hence small shifts in peak positions are observed.

$[Co(NH_3)_5N_3]Cl_2$ is the only exception since a red shift of 550 cm^{-1}, with respect to ν_{max} in water, has been observed[4] in 90% glycerol. This is significantly greater than the observed red shift 210 cm^{-1} in DMSO. As the dielectric constant of the two media are nearly equal, it is probable, that some sort of specific interaction is occurring involving a charge transfer from solvent[4] to Co(III), as both glycerol and DMSO are more easily oxidisable than water.

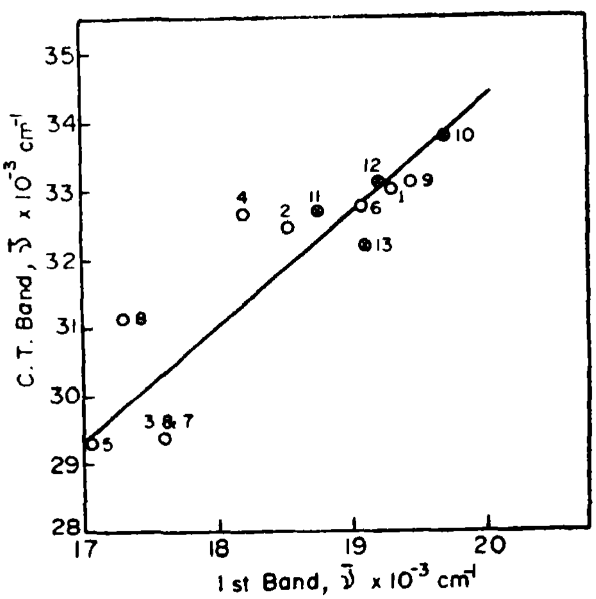
A possible explanation for the exceptional behaviour of $[Co(NH_3)_5N_3]Cl_2$ may be due to its high cationic charge, being the largest amongst the series of compounds studied. For highly charged cations the scope of solute solvent interactions is widened to include medium components of lower polarity (glycerol). For lower cationic charge, propensity for interaction with components of lower polarity in a mixed solvent medium, is less or at least small enough to have no effect on the spectra.

A correlation is observed between CTTM bands and the ligand band when the complex does not contain any highly electronegative and/or strongly back bonding ligand (Fig. 4).

A linear relationship is found to exist between the wave number of charge transfer bands and those of the first band (Table 2). Similar relationships were also found[7] for singlet and triplet transitions for complexes of cobalt(III). This implies that the bands originate from and terminate at orbitals which are similar in nature. For ligands like azido, which have an extra lone pair of electrons available[8], after forming σ bonds with the metal, the charge transfer band is of type $e_g \leftarrow \pi$, i.e., from a π

TABLE 2

Sl. No.	Compound	1st Band	3rd Band	Solvent	Reference
1.	$[Co(NH_3)_5N_3]Cl_2$		33000	Water	This work
		19280		Water	14
2.	*cis*$[Co(NH_3)_4(N_3)_2]N_3$	18520	32470	NaOAc/HOAc buffer of *p*H 4	This work
2A.	*cis*$[Co(NH_3)_4(N_3)_2]ClO_4$	18580		Water	7
3.	*trans*$[Co(NH_3)_4(N_3)_2]N_3$	17610	29410	Phthalate buffer *p*H 4	This work
		17610		Water	7
4.	*cis*$[Co(NH_3)_3(N_3)_3]$	18180	32680	DMSO + H_2O	This work
5.	*trans*$[Co(NH_3)_3(N_3)_3]$	17060	29330	DMSO + H_2O	This work
		16900		DMSO	2
6.	*cis*$[Co(en)_2(N_3)_2]ClO_4$	19080	32790	Water & buffer of *p*H 4	This work
		19050	32680	Water	8
7.	*trans*$[Co(en)_2(N_3)_2]ClO_4$	17610	29410	Water & buffer of *p*H 4	This work
		17650	29500	Water	8
8.	*trans*$[Co(en)_2N_3Cl]ClO_4$	17300	31150	Water & buffer of *p*H 4	This work
		17310	31250	Water	8
9.	*trans*$[Co(Dipy)_2(N_3)_2]ClO_4.2H_2O$	19460	33110	Water	This work
9A.	*trans*$[Co(Dipy)_2(N_3)_2]N_3.2H_2O$	19400		Water	12
10.	*cis*$[Co(en)_2N_3SCN]_2S_2O_6$	19690	33780	Water	11
11.	*trans*$[Co(en)_2N_3SCN]ClO_4$	18740	32680	Water	11
12.	*cis*$[Co(en)_2NH_3N_3]S_2O_6$	19180	33110	Water	11
13.	*cis*$[Co(en)_2N_3Cl]ClO_4$	19100	32200	Water	8



Plot of C.T. Band vs. First Band

● data from literature ,

○ data from this work .

Fig. 4

molecular orbital localised at the ligand to the anti-bonding e_g orbitals of the metal[9,10]. Progressive substitution by more azido groups do not affect the overall symmetry of the complex as the ligand bands do not undergo any splitting.

In complexes such as *cis* and *trans* $[Co(en)_2N_3NO_2]ClO_4$ where bands other than the first and third occur[11] this linear relationship does not hold. This is also true for bisazido *o*-phenanthroline complex[12]. Since the third and first band of bisazido bipyridyl complex[12], falls on this line, it is quite probable that the assignment of these bands in this complex is similar to the other azido complexes of cobalt(III). Such a correlation is not found for the u.v. and visible bands of *cis* and *trans* $[Co(big\ H)_2](N_3)_2]N_3.H_2O$, the synthesis and spectral characteristics of which were reported[13] in part I.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 809-812

Kinetics of Silver Catalysed Oxidation of N-Methyl Acetamide by Potassium Peroxydisulphate

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Manuscript received 15 June 1978, revised 18 March 1980, accepted 21 May 1980

The kinetics of silver catalysed oxidation of N-methyl acetamide by peroxydisulphate ion in aqueous medium has been investigated. The reaction is found to be first order w.r.t. $S_2O_8^{-2}$; zero order w.r.t. N-methyl acetamide but the specific rate is function of $S_2O_8^{-2}$ and $CH_3CONHCH_3$ concentrations. It decreases with an increase in $S_2O_8^{-2}$ concentration but increases with an increase in $CH_3CONHCH_3$ concentration and becomes immeasurable at high concentrations. The specific rate is linearly related to $[Ag^+]$ ion by an expression.

$$K = 3.60\times10^{-4} + 0.40\times C_{Ag^+}$$

K^+ exerts a strong inhibitory effect on the rate. The temperature coefficient, energy of activation, frequency factor and entropy of activation have been calculated. The molecular ratio is found to be 2 : 1. The final products of the system are CH_3COOH, CO_2, N_2 and H_2O. On the basis of these results a possible reaction mechanism has been proposed and a corresponding rate expression has been deduced.

Peroxydisulphate ion has only been used to bring about the oxidation of several classes of organic substrates and the kinetics of some of the processes have been dealt by different workers. These studies up to 1962 have been reviewed by House[1]. The noteworthy work done may be cited as oxidation of oxalic acid[2-4] and of alcohols[5-8]. However, only recently the kinetic study of oxidation of amides by peroxydisulphate ion has been carried out by Mushran and coworkers[9,10] and by Srivastava and Singh[11-14]. The present paper contains the results of kinetic study of silver catalysed oxidation of N-methyl acetamide by peroxydisulphate ion in an aqueous medium.

Experimental

The experimental technique of dimethyl formamide-peroxydisulphate reaction[11] has been adopted in this case as well. Blank estimation of peroxydisulphate ion in presence of N-methyl acetamide was first done to test the sensitivity of this method in this procedure.

Results

As in the reactions of dimethyl formamide[11] and propionamide[12] the specific rate (k) for N-methyl acetamide oxidation in each kinetic run was determined by subtracting the specific rate (k_2) for self decomposition of potassium peroxydisulphate, carried out under similar conditions from the rate (k_1) for the total reaction. The kinetic results obtained at various concentrations of reactants are given graphically in Figs. 1 and 2 and are tabulated in Table 1.

It may easily be concluded from the table that the first order specific rate is function of peroxydisulphate ion as well as N-methyl acetamide concentration; it decreases with an increase in peroxydisulphate ion concentration and is governed by the expression

$$-\log k = 2.325 + 6.80\,[S_2O_8^{-2}]_0$$

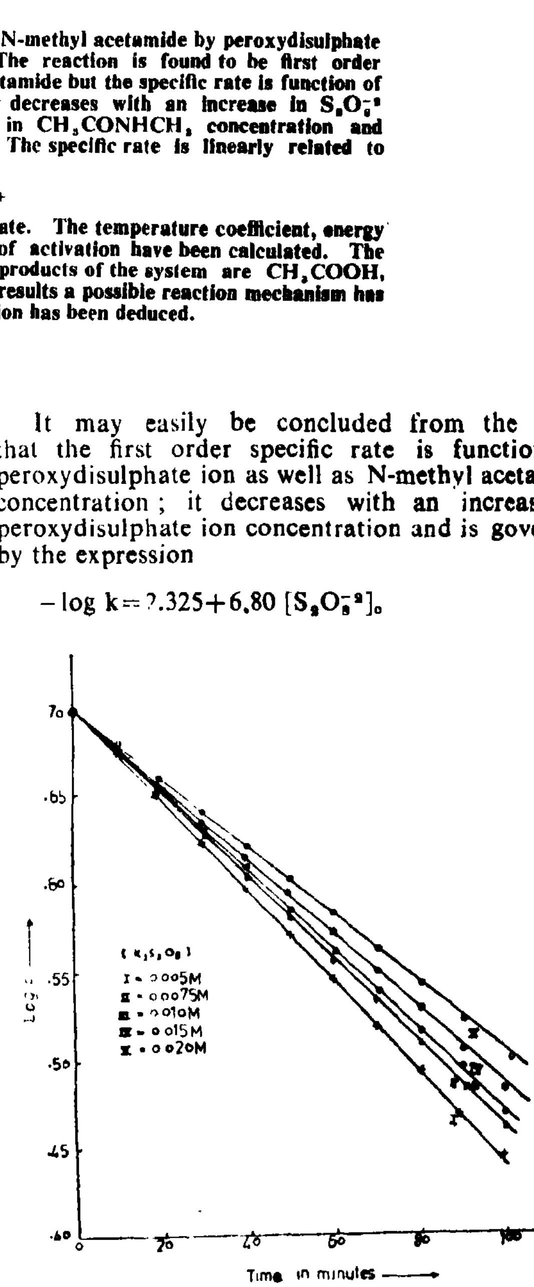


Fig. 1. Effect of $K_2S_2O_8$ concentration: $[CH_3CONHCH_3]=0.05M$; $[AgNO_3]=0.001M$; Temp. = 35°C.

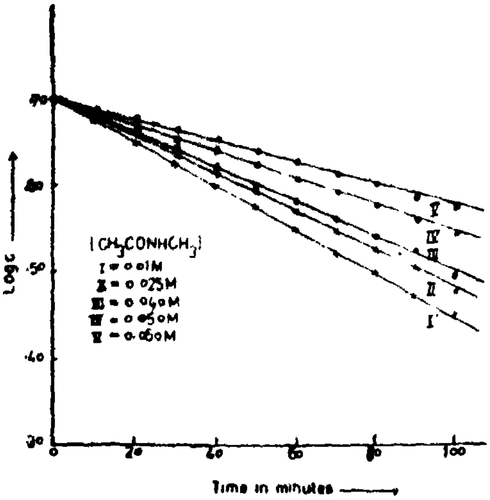


Fig. 2. Effect of $CH_3CONHCH_3$ concentration.
$[K_2S_2O_8] = 0.01M$, $[AgNO_3] = 0.001M$, Temp. = 35°C

TABLE 1

$[AgNO_3] = 1 \times 10^{-3}M$ Temp. = 35°C

$[K_2S_2O_8]$ Conc.	$[CH_3CONHCH_3]$ Conc.	$k_1 \times 10^3$ min^{-1}	$k_2 \times 10^3$ min^{-1}	$k \times 10^3 = (k_1 - k_2)$ min^{-1}
0.0050M	0.050M	6.06	1.70	4.36
0.0075M	0.050M	5.62	1.44	4.18
0.010M	0.050M	5.33	1.34	3.99
0.015M	0.050M	5.00	1.21	3.79
0.020M	0.050M	4.61	1.15	3.46
0.010M	0.010M	3.03	1.34	1.69
0.010M	0.025M	3.84	1.34	2.50
0.010M	0.040M	4.70	1.34	3.36
0.010M	0.050M	5.90	1.34	4.56

whereas it increases in a linear manner with an increase in N-methyl acetamide concentration and obeys the following relationship :

$$k = 1.08 \times 10^{-4} + 8.0 \times 10^{-2}[CH_3CONHCH_3]_0$$

The above findings are similar to those obtained in oxidation of alcohols[6-9] and dimethyl formamide[11] by peroxydisulphate ion.

Effect of $AgNO_3$ concentration : The effect of silver nitrate has been studied by carrying out the experiments at different concentrations of $AgNO_3$ as shown in Table 2.

TABLE 2

$[K_2S_2O_8] = 0.01M$, $[CH_3CONHCH_3] = 0.05M$ Temp. = 35°C

$[AgNO_3] \times 10^3 M$	$k_1 \times 10^3$ min^{-1}	$k_2 \times 10^3$ min^{-1}	$k \times 10^3$ min^{-1} $(k_1 - k_2)$
1.00	5.33	1.34	3.99
1.50	6.14	1.98	4.16
2.00	6.87	2.46	4.41
2.50	7.80	3.20	4.60
3.00	8.69	3.90	4.79

The catalytic effect of $AgNO_3$ is similar to that obtained in dimethyl formamide[11] and propionamide[12] reactions and following relationship holds good :

$$K = 3.60 \times 10^{-3} + 0.40\, C_{Ag^+}$$

Effect of Temperature : The reaction was studied at four different temperatures for the evaluation of various energy parameters, the results are summarized in Table 3.

TABLE 3

$[K_2S_2O_8] = 0.01M$, $[AgNO_3] = 0.001M$, $[CH_3CONHCH_3] = 0.05M$

Temp. in °A	$K \times 10^3$ min^{-1}	Temp. coefficient	Energy of activation (ΔE) in K cals mole^{-1}	Frequency factor $A \times 10^7$ in lit mole^{-1} sec^{-1}	Entropy of activation (ΔS$^{\neq}$) in E.U.	Free energy (ΔG$^{\neq}$) in K cals mole^{-1}
303	2.52			10.82	−24.23	23.80
308	3.98	2.51	17.32	10.53	−24.23	23.93
313	6.33	2.44	17.08	10.55	−24.24	24.04
318	9.70			10.69	−24.22	24.17
Mean		2.47	17.20	10.65	−24.23	23.98

E graphically came out to be 16.35 K cals mole^{-1}.

$\Delta H^{\neq}$ was calculated by plot of $\log \frac{k}{kT/h}$ vs $(1/T)$ on the basis of

$$k = \frac{kT}{h} \times e^{-\Delta H^{\neq}/RT} \times e^{\Delta S^{\neq}/R}$$

The value of $\Delta H^{\neq}$ which came out to be 16.47 K cals mole^{-1} has been used in the above equation to calculate $\Delta S^{\neq}$.

The large negative entropy of activation is indicative of incorporation of water molecule (reaction mechanism, equation 2) and the involvement of two oppositely charged ions (reaction mechanism, equation 1) during the course of reaction[11-12]. Further it may be mentioned that the energy of activation and negative entropy of activation for this reaction are of the similar order of magnitude as that for the oxidation of dimethyl formamide[11] and propionamide[12].

Salt effect and specific effect of ions : In order to study the dependence on ionic strength (μ) the reaction was studied at various concentrations of the salt K_2SO_4. It was observed that the specific rate constant decreases by the increase in ionic strength. Further a plot between log k vs $\mu^{1/2}$ was found to be a straight line which establishes a negative salt effect on the reaction. The specific effect of K^+, Na^+, H^+ and Zn^{++} ions were studied. The results of these studies are tabulated in Table 4.

TABLE 4

$[K_2S_2O_8] = 0.01M$, $[CH_3CONHCH_3] = 0.05M$, $[AgNO_3] = 0.001M$

Temp. = 35°C

Salt added	Conc.	$k_1 \times 10^3$ min^{-1}	$k_2 \times 10^3$ min^{-1}	$k \times 10^3$ min^{-1} = $(k_1 - k_2)$
—	—	5.33	1.34	3.99
K_2SO_4	0.04*M*	2.98	0.88	1.90
Na_2SO_4	0.04*M*	3.11	0.98	2.15
H_2SO_4	0.04*M*	3.39	1.09	2.30
$ZnSO_4$	0.04*M*	3.49	1.15	2.84

It is evident from above data that of all the ions under study K^+ has strong specific inhibitory effect on the rate.

Effect of Allyl Acetate : To study the effect of organic compounds on reaction rate, the allyl acetate was chosen. Fig. 3 consists of the effect of traces of allyl acetate on the rate of N-methyl acetamide reaction and self decomposition of peroxydisulphate ion. It is obvious that the inhibitory effect on the two reactions is of similar order of magnitude indicating that the radical(s) involved in the self decomposition and N-methyl acetamide oxidation would have been the same.

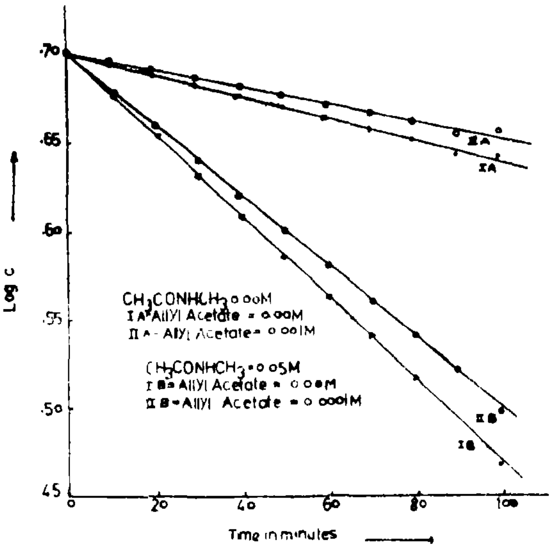


Fig. 3. Effect of allyl acetate : $[K_2S_2O_8] = 0.01M$; $[AgNO_3] = 0.0001M$; Temp = 35°C.

Mole ratio and Products of reaction : The mole ratio between peroxydisulphate ion and N-methyl acetamide, after taking into consideration the decomposition of $S_2O_8^{-2}$ comes out to be 2 moles of $S_2O_8^{-2}$ to one mole of $CH_3CONHCH_3$. The presence of acetic acid throughout the course of reaction was detected by conventional tests. On the other hand, the presence of methyl amine, formaldehyde, formic acid and ammonia (detected by Reiglers reagent[15]) was observed in the early stages only and after 24 hours none of these were found to be present, probably due to their oxidation to N_2, CO_2 as final products of the system. The presence of NH_3, HCHO and HCOOH indicates that CH_3NH_2 formed in the beginning suffers decomposition to methyl-enimin ($CH_2=NH$) and later into NH_3, HCHO, HCOOH. The formation of methyl-enimin as intermediate product in the preparation of primary amines by reactions of aldehydes and ketones with ammonia has also been mentioned by Morisson and Boyd[16].

Discussion

The first order behaviour of reaction w.r.t. $S_2O_8^{-2}$, zero order w.r.t. $CH_3CONHCH_3$ linear relationship between specific rate and Ag^+, strong specific inhibitory effect of K^+, mole ratio 2 : 1 between $S_2O_8^{-2}$ and $CH_3CONHCH_3$ and N_2, CO_2 and H_2O being the final products, suggest that the following reaction mechanism may be possible.

$$S_2O_8^{-2} + Ag^+ \xrightarrow{k_1} Ag^{+2} + SO_4^{-2} + SO_4^- \quad \ldots (1)$$

$$H_2O + SO_4^- \xrightarrow{k_2} HSO_4^- + .OH \quad \ldots (2)$$

$$CH_3CONHCH_3 + H_2O \underset{-k_3}{\overset{k_3}{\rightleftharpoons}} CH_3COOH + CH_3NH_2 \quad \ldots (3)$$

$$CH_3NH_2 + .OH \xrightarrow{k_4} CH_2 = NH + H_2O + H^+ \quad \ldots (4)$$

$$CH_2 = NH + H_2O \xrightarrow{k_5} HCHO + NH_3 \quad \ldots (5)$$

$$HCHO + .OH \xrightarrow{k_6} HCOOH + .H \quad \ldots (6)$$

$$.H + SO_4^- \xrightarrow{k_7} HSO_4^- \quad \ldots (7)$$

$$HCOOH + .OH \xrightarrow{k_8} HCOO. + H_2O \quad \ldots (8)$$

$$HCOO. + SO_4^- \xrightarrow{k_9} HSO_4^- + CO_2 \quad \ldots (9)$$

$$NH_3 + Ag^{+2} \xrightarrow{k_{10}} .NH_2 + Ag^+ + H^+ \quad \ldots (10)$$

$$.NH_2 + .OH \xrightarrow{k_{11}} .NH + H_2O \quad \ldots (11)$$

$$.NH + .OH \xrightarrow{k_{12}} \tfrac{1}{2}N_2 + H_2O \quad \ldots (12)$$

It is noteworthy to mention here that the first two steps have been proposed by Bown and Margerison[17] and Srivastava and Singh[11-13] in silver catalysed oxidation reactions by peroxydisulphate ion.

Applying the steady state treatment to the radicals Ag^{+2} SO_4^- ; $.NH_2$; .NH ; .OH ; .H and HCOO. and also keeping in mind that the rate of disappearance of $S_2O_8^{-2}$ is governed by process (1), the rate of reaction has been simplified to

$$\frac{-d[S_2O_8^{-2}]}{dt}=k[S_2O_8^{-2}][Ag^+]$$

where k is the experimental first order rate constant.

The above equation is in conformity with experimental results and the mechanism elucidated.

Acknowledgement

The research facilities given by Dr. S. S. Gupta, Principal, D. S. College, Aligarh are gratefully acknowledged. We are also thankful to U. G. C. for providing financial assistance to carry out this work.

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Indian Chem. Soc.,
ol. LVII, August 1980, pp. 813-815

Conductance Studies in Multicomponent Solutions Involving Electrolytes

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Manuscript received 20 November 1979, revised 2? March 1980, accepted 21 May 1980

Electrical conductance, in water, determined at 30°, have been used to calculate activity coefficient and dissociation constants in multicomponent solutions. Electrical conductance at infinite dilution have been used as measure of solute-solvent interaction. The activity coefficient is found to increase more rapidly with concentration. Dissociation constant shows that association in the case of lithium chloride is greater than in case of sodium chloride and potassium chloride.

ELECTRICAL conductance have been used as a measure of solute-solvent interaction[1-6]. The solute-solvent interaction that has received a great importance have also been studied from the estimation of properties like molar volume[7-11], free energy of transfer[12-14] and viscosity[15-19]. Literature is full of such studies as single component solutions in water but investigations in multi-component solutions involving mixed solvent is scanty. Recently Padova *et al*[20] have determined activity coefficients in aqueous quaternary system NaCl - KCl - $MgCl_2$ from isopiestic measurements at 25°. Concentrated solutions 0.2 *M* – 0.8 *M* have been used for investigation. Equivalent conductance at infinite dilution being calculated from equation due to Robinson and Stokes[27]. The object of study is to investigate solute-solvent interaction in multi-component solutions that play important role in physiological processes and cell equilibria in both plants and animals.

Experimental

Materials : Water needed for preparation of various solutions was prepared by distilling thrice, over alkaline $KMnO_4$. The specific conductance of water thus prepared was 1.3×10^{-6} $ohm^{-1}cm^{-1}$. Electrolytes viz., potassium and sodium chloride were of AnalaR grade and were used without further purification. Lithium chloride (BDH) was purified by recrystallising from water and dried for 24 hours at 130° in an oven. Every electrolyte was kept over P_2O_5 in vacuum desiccator before use.

Procedure : All solutions were made by weight and conversion of molality to molarity was carried out by expression[22]. Conductance[23] and density[24] measurements were carried out by methods described in our earlier publications. All measurements made in thermostat have fluctuation in temperature less than $\pm0.05°$. The standard deviation in density and conductance measurements are ±0.000011 gm. cm^{-3} and ±0.04 $ohm^{-1}cm^{2}mol^{-1}$ respectively.

Results and Discussion

Equivalent conductance at infinite dilution was calculated from the equation due to Robinson and Stokes[27].

$$\Lambda = \Lambda_0 - \left[\frac{az_1z_2q\Lambda_0}{1+q^{\frac{1}{2}}}+b(z_1+z_2)\right]\cdot\frac{I^{\frac{1}{2}}}{1+Ba^{\circ}I^{\frac{1}{2}}} \quad \ldots \quad (1)$$

Here Λ = Equivalent conductance of solution

Λ_0 = Equivalent conductance at infinite dilution

z_1, z_2 = Charge no. of ions (cation and anion)

a, b = Constants

I = Total ionic strength

a° = Closest distance of approach

B = Constant having value 0.33 approx. at 30°.

The value of Λ_0 was determined from the intercept of plot Λ versus $I^{\frac{1}{2}}/1+Ba^{\circ}I^{\frac{1}{2}}$. The constant a° was arbitrarily adjusted to give the best fit. The value varied from 3-5Å.

The value of dissociation constant suggests that there is partial association. The values of Λ_0 were also calculated from Owen's plots[25]. The approximate value being taken from Λ versus $\sqrt{C}$ plots.

The values of limiting equivalent conductance determined from the two methods is recorded in Table 1 alongwith the value of dissociation constant.

The order of magnitude of Λ_0 for varied solutions is as follows :

KCl > NaCl > LiCl

But the value of dissociation constant shows that

TABLE 1—LIMITING EQUIVALENT CONDUCTANCE AND DISSOCIATION CONSTANTS FOR MULTICOMPONENT SOLUTIONS AT 30°C

System	Λ_0 (Robinson and Stokes) ($ohm^{-1}cm^2mol^{-1}$)	Λ_0 (Owen's) ($ohm^{-1}cm^2mol^{-1}$)	K Dissociation Constant × 10
0.01 *M* KCl + NaCl(C)	121.1	127.9	3.47
0.01 *M* KCl + LiCl(C)	119.5	118.9	3.69
0.01 *M* LiCl + KCl(C)	173.2	172.0	1.95
0.01 *M* LiCl + NaCl(C)	122.5	124.4	3.62
0.01 *M* NaCl + KCl(C)	176.8	170.2	0.50
0.01 *M* NaCl + LiCl(C)	118.5	112.5	0.29
0.01 *M* LiCl + 0.01 *M* NaCl + KCl(C)	180.1	190.0	0.48
0.01 *M* KCl + 0.01 *M* LiCl + NaCl(C)	134.2	139.5	1.12
0.01 *M* KCl + 0.01 *M* NaCl + LiCl(C)	132.0	123.2	0.17

the order of association is :

LiCl > KCl > NaCl

Li^+ ion being highly hydrated and showing more association than others, is less mobile and hence shows less equivalent conductance at infinite dilution than others. KCl shows more association than NaCl, the greater limiting equivalent conductance may be due to the greater mobility of K^+[26]. Since Λ_0 have been regarded as measure[27] of solute-solvent interaction, the greater value in a particular solvent may therefore be interpreted in terms of greater ion-solvent interactions. Limiting equivalent conductance was used to calculate the degree of dissociation of varied solutions. The activity coefficient was then calculated using equation[27] :

$$-\log f = \frac{A(\sqrt{\alpha C})}{1+Ba(\sqrt{\alpha C})} \qquad \ldots \quad (2)$$

where f = activity coefficient

α = degree of dissociation

C = molar concentration

a = closest distance of approach

A and B are constants.

The value of A and B at 30° was determined from plots A versus temperature and B versus temperature respectively as they increase linearly with temperature[28].

Ignoring the small difference between f and γ, the f value was used to calculate the dissociation constant by equation[27] :

$$K = \frac{\alpha^2\gamma^2 C}{(1-\alpha)} \qquad \ldots \quad (3)$$

Table 2 shows the values of activity coefficient for different solutions and we find that the value of activity coefficient increases with concentration. Further the value of activity coefficient has the following order :

NaCl > KCl > LiCl

The reasons for this order may be the order of association.

TABLE 2—ACTIVITY COEFFICIENT VALUES FOR DIFFERENT SOLUTIONS OF MULTICOMPONENT SYSTEMS AT 30°C

Molarity C × 10³ (mol. l^{-1})	Activity Coefficient (f)
Solute : NaCl; Solvent : 0.01 *M* KCl in water	
9.932	0.240
19.848	0.297
29.724	0.331
9.589	0.356
58.994	0.390
78.938	0.413
Solute : LiCl; Solvent : 0.01 *M* KCl in water	
9.928	0.228
19.811	0.267
29.651	0.299
39.471	0.322
58.919	0.343
78.169	0.360
Solute : KCl; Solvent : 0.01 *M* LiCl in water	
9.955	0.234
29.696	0.320
39.470	0.345
58.703	0.378
78.044	0.394
Solute : NaCl; Solvent : 0.01 *M* LiCl in water	
19.931	0.295
29.800	0.330
39.579	0.357
59.194	0.389
78.630	0.412
Solute : KCl; Solvent : 0.01 *M* NaCl in water	
19.803	0.277
29.612	0.306
39.379	0.325
58.801	0.353
77.986	0.375

(Table 2 Contd.)

Solute : LiCl Solvent : 0.01 *M* NaCl in water	
9.932	0.220
29.633	0.293
39.474	0.312
58.971	0.336
78.170	0.353
Solute : KCl Solvent : 0.01 *M* LiCl+0.01 *M* NaCl in water	
19.859	0.277
29.683	0.298
39.471	0.323
58.908	0.360
78.119	0.371
Solute : NaCl Solvent : 0.01 *M* KCl+0.01 *M* LiCl in water	
19.917	0.285
29.781	0.318
39.632	0.337
59.203	0.368
78.651	0.389
Solute : LiCl Solvent : 0.01 *M* NaCl+0.01 *M* KCl in water	
9.955	0.218
19.857	0.263
29.706	0.287
39.519	0.304
58.968	0.330
78.287	0.346

Acknowledgement

One of the authors (Satish Kumar) is thankful to CSIR, New Delhi for award of JRF in the scheme.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 816-818

Relative Efficacies of Cationic and Anionic Surfactants and Their Mixtures in the Suppression of Polarographic Negative Maximum of Ni(II)

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Manuscript received 19 April 1979, accepted 27 May 1980

The suppression of polarographic negative maximum of Ni(II) has been attempted by various cationic and anionic surfactants viz., Lauryl pyridinium chloride (LPC), Cetyl pyridinium chloride (CPC), Cetyl pyridinium bromide (CPB), Cetyl trimethylammonium bromide (CTAB), Cetyl dimethyl benzyl ammonium chloride (CDBAC), Sodium lauryl sulphate (SLS), Dodecyl benzene sulphonate (DBS), Dioctyl sodium sulpho-succinate (DSSS), Dibutyl sodium sulpho-succinate (DBSS) and Tergitol-7. The relative efficacies of these surfactants and their mixtures have been established on the basis of the value of the kinetic parameter 'αn_a' calculated by Koutecky's method. A comparison of 'αn_a' values at the stage where maximum just disappears gives the relative efficacies of cationic and anionic surfactants and also an insight into their additive or antagonistic influence in the mixture.

RAM *et al*[1,2] have reported the suppression of polarographic maxima of Ni(II) and Co(II) by various ionic and non-ionic surfactants and have compared their relative efficacies on the basis of characteristic properties viz., maximum suppression point[3] (*M.S.P.*), specific suppression coefficient[4] (S.S.C.) and critical micelle concentration[5] (C.M.C.). Dubey *et al*[6] have studied the effect of increasing concentrations of some ionic and non-ionic surfactants beyond the concentration just sufficient to eliminate the maxima on the kinetics of the electrode reactions of Ni(II) and Co(II). Recently, Singh and coworkers[6] have compared the efficacies of some heavy metal cations in the suppression of Ni(II) maximum in terms of kinetic parameter 'αn_a'. However, the efficacies of ionic and non-ionic surfactants in the suppression of Ni(II) maximum have not been investigated quantitatively so far. Moreover, according to Kuta[7] very interesting results can be obtained if two surfactants of opposite sign are used as suppressors in mixture. Therefore, in the present study an attempt has been made to compare the efficacies of ionic and non-ionic surfactants separately as well as their mixtures.

Experimental

All the chemicals used were of A.R., B.D.H. grade and their solutions were prepared in conductivity water. The depolarizer concentration was kept at $2.0\times10^{-3}M$. $NaNO_3$ (0.05*M*) was used as the supporting electrolyte.

A manual polarograph (Toshniwal CL 02) in conjunction with a polyflex galvanometer (Toshniwal PL 50) was used for measuring the potential and current respectively. Deoxygenation of the solutions was done by passing through the solution a steady stream of purified nitrogen gas. All the measurements were made at 25±0.1°. Saturated calomel electrode (S.C.E.) was used as a reference electrode. The d.m.e. had the following characteristics:

$m = 1.67$ mg/sec, $t = 4.04$ sec, $m^{2/3}t^{1/6} = 1.778$ $mg^{2/3}\ sec^{-1/2}$, $h_{corr} = 63.0$ cm.

Results and Discussion

On being suppressed by the requisite amounts of the surfactants, Ni(II) yields, in each case, a well-defined diffusion-controlled wave. On applying various criteria of irreversibility[8-11], it has been ascertained that the electrode reaction of Ni(II) is totally irreversible in the presence of different amounts of cationic and anionic surfactants as well as in their mixtures. The value of the kinetic parameter αn_a has been calculated by Koutecky's method[12].

From Table 1 it is evident that αn_a shows a decrease with increase in the concentration of each surfactant. αn_a values (and subsequent estimation of α) give a measure of the extent to which kinetics of the electrode reaction is being influenced. An attempt to estimate n_a (the number of electrons involved in the rate determining step) leads to a conclusion that n_a is equal to 2. However, according to Meites[13] only a single electron can be transferred at a time and a value of n_a exceeding 1 would not necessarily mean that two electrons are actually

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TABLE 1—POLAROGRAPHIC CHARACTERISTICS OF Ni(II) IN THE PRESENCE OF INCREASING CONCENTRATIONS OF CATIONIC AND ANIONIC SURFACTANTS

Surfactants	[Surfactant] M	i_d μA	$-E_{1/2}$ V (S.C.E.)	D × 10^6 cm²/sec	αn_a
Cationic					
LPC	*4.0×10^{-7}	12.09	1.08	5.81	0.64
	1.0×10^{-6}	11.62	1.09	5.33	0.46
CPC	*4.0×10^{-7}	11.93	1.08	5.64	0.53
	1.0×10^{-6}	11.62	1.09	5.33	0.46
CPB	*5.4×10^{-6}	10.99	1.03	4.79	0.53
	7.0×10^{-6}	10.05	1.04	4.00	0.47
CTAB	*8.0×10^{-6}	11.62	1.11	5.33	0.57
	1.0×10^{-5}	8.79	1.17	3.06	0.53
CDBAC	*8.0×10^{-6}	11.40	1.07	5.15	0.49
	4.8×10^{-5}	9.88	1.13	3.87	0.47
Anionic					
SLS	*2.0×10^{-4}	11.77	1.10	5.49	0.59
	1.0×10^{-3}	10.52	1.14	4.39	0.53
DBS	*1.0×10^{-4}	12.87	1.12	6.55	0.4[illegible]
	1.0×10^{-3}	12.56	1.15	6.25	0.43
Tergitol-7	*4.0×10^{-7}	12.54	1.09	6.23	0.64
	1.0×10^{-6}	12.16	1.10	5.85	0.57
DSSS	*7.0×10^{-5}	14.23	1.13	8.82	0.46
	1.0×10^{-4}	13.19	1.15	7.62	0.43
DBSS	*6.0×10^{-3}	15.38	1.14	8.00	0.61
	1.6×10^{-2}	13.81	1.20	7.56	0.59

* indicates the concentration of surfactant at which the maximum just disappears.

added simultaneously but merely that the successive steps are too nearly simultaneous to be distinguished on the time scale implicit in the polarographic measurement. Since the decrease in αn_a values is indiscrete and at no stage the two consecutive values vary by a factor of 2, the possibility of decrease in the value of the product αn_a due to the change in n_a is ruled out. Thus it can be safely concluded that it is α which is decreasing[14]. α, the transfer coefficient signifies[15] the fraction of the applied voltage which favours the cathodic reaction, $Ni^{2+} + 2e \longrightarrow Ni$. A decrease in the value of α thus implies that the transfer of electron/electrons is made increasingly difficult. In other words, the electrode reaction of Ni(II) is rendered increasingly more irreversible. A decrease in i_d and a negative shift in $E_{1/2}$ with an increase in the concentration of both cationic and anionic surfactants lend support to this conclusion.

Relative efficacies of surfactants in terms of αn_a values

At the stage where maximum of Ni(II) just disappears, the order of αn_a values signifies the extent to which the addition of cationic and anionic surfactants renders the electrode reaction more irreversible from the position in the absence of these surfactants. In other words, a surfactant for which αn_a has got higher value at the point of just suppression will be more effective with minimum influence on the kinetics of the electrode reaction. In the present study the order of αn_a values for different surfactants is as follows :

Cationic : LPC > CPC, CPB > CTAB > CDBAC
Anionic : Tergitol-7 > DBSS, SLS > DBS > DSSS

Thus among the cationic surfactants LPC eliminates

TABLE 2—POLAROGRAPHIC CHARACTERISTICS OF Ni(II) IN THE PRESENCE OF MIXTURES OF CATIONIC AND ANIONIC SURFACTANTS

Cationic + Anionic surfactants	[Cationic + Anionic] M	i_d μA	$-E_{1/2}$ V (S.C.E.)	D × 10^6 cm²/sec	αn_a
LPC + SLS	*$2.0 \times 10^{-7} + 1.0 \times 10^{-4}$	12.25	1.04	5.95	0.81
	$1.0 \times 10^{-6} + 1.0 \times 10^{-3}$	11.6	1.07	5.33	0.74
LPC + DBS	*$4.0 \times 10^{-7} + 8.0 \times 10^{-5}$	12.56	1.09	7.10	0.67
	$1.0 \times 10^{-6} + 1.0 \times 10^{-4}$	12.24	1.10	6.72	0.43
CPC + Tergitol-7	*$4.0 \times 10^{-8} + 2.0 \times 10^{-7}$	13.34	1.09	7.02	0.64
	$6.0 \times 10^{-9} + 4.0 \times 10^{-7}$	12.56	1.10	6.25	0.49
CPB + DSSS	*$4.4 \times 10^{-6} + 6.0 \times 10^{-5}$	12.87	1.12	6.55	0.51
	$7.0 \times 10^{-6} + 1.0 \times 10^{-4}$	12.56	1.21	6.25	0.43
CPC + DSSS	*$4.0 \times 10^{-7} + 7.0 \times 10^{-5}$	12.56	1.12	5.95	0.51
	$1.0 \times 10^{-6} + 1.0 \times 10^{-4}$	11.30	1.15	5.06	0.49
CPB + Tergitol-7	*$5.0 \times 10^{-7} + 0.5 \times 10^{-7}$	12.56	1.13	6.25	0.55
	$5.0 \times 10^{-6} + 1.5 \times 10^{-6}$	10.83	1.16	6.65	0.47
CTAB + DSSS	*$1.0 \times 10^{-7} + 1.0 \times 10^{-4}$	12.56	1.13	6.25	0.67
	$6.0 \times 10^{-7} + 6.0 \times 10^{-4}$	11.30	1.15	5.06	0.57
CTAB + Tergitol-7	*$0.5 \times 10^{-7} + 0.5 \times 10^{-7}$	12.54	1.10	6.23	0.64
	$1.0 \times 10^{-6} + 1.0 \times 10^{-6}$	11.40	1.13	5.15	0.57
CDBAC + DSSS	*$3.0 \times 10^{-6} + 6.0 \times 10^{-5}$	13.50	1.14	7.23	0.55
	$1.3 \times 10^{-5} + 2.0 \times 10^{-4}$	7.69	1.21	2.34	0.46
CDBAC + Tergitol-7	*$1.5 \times 10^{-6} + 1.5 \times 10^{-7}$	15.70	1.06	9.73	0.61
	$2.5 \times 10^{-5} + 2.5 \times 10^{-6}$	14.76	1.07	8.64	0.47
CDBAC + DBSS	*$1.5 \times 10^{-6} + 3.0 \times 10^{-3}$	14.76	1.09	8.64	0.64
	$1.2 \times 10^{-5} + 2.3 \times 10^{-2}$	13.66	1.18	7.39	0.61

* indicates the concentration of surfactant at which the maximum just disappears.

the maximum of Ni(II) with minimum influence on the kinetics of the electron transfer followed by CPC, CPB, CTAB and CDBAC. On the other hand, among the anionic surfactants DBSS eliminates the maximum with minimum influence of the kinetics of the electron transfer followed by Tergitol-7, SLS, DBS and DSSS.

A comparison of αn_a values at the point of just suppression in respect of the mixtures of cationic and anionic surfactants shows that their effect is additive in suppressing the maximum except for the mixture of CPB and DSSS where the effect has been found to be antagonistic.

Acknowledgement

Thanks are due to Dr. S. N. Srivastava, Principal, Agra College, Agra for facilities.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 819-822

Thermodynamics of Cation Exchange in Tantalum Arsenate

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Manuscript received 4 December 1978, revised 14 February 1980, accepted 13 May 1980

The equilibrium exchange of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+} and Th^{4+} ions with the hydrogen form of tantalum arsenate at a constant ionic strength of 0.1*N* in the reaction :

$$_{n}RH+M^{n+} \rightleftharpoons R_{n}M+nH^{+}$$

has been studied. Solid phase activity coefficients for the exchanging ions and free energy changes have been evaluated from the ion-exchange isotherms. The enthalpies of reaction and the corresponding entropy values were calculated. The thermodynamic functions for different cations depend upon the hydrated radii of ingoing cation.

A number of studies of the temperature dependence of ion exchange reaction on synthetic organic resins have been reported[1,2,3,4]. Inorganic ion exchangers are also being developed with great interest and their respective studies are in order. Zirconium phosphate has been studied in greater detail[5] as a synthetic inorganic ion exchanger. Larsen[6] studied the equilibria of Li^{+}-H^{+}, Na^{+}-H^{+} and K^{+}-H^{+} on zirconium phosphate. Baetsle[7] studied the tracer ion equilibria on zirconyl phosphate in hydrogen form with Rb^{+}, Cs^{+}, Sr^{2+}, Ce^{3+} and Eu^{3+}. Nancollas[8] determined the equilibrium exchange of Li^{+}, K^{+} and Cs^{+} ions with the hydrogen form of semicrystalline zirconium phosphate at a constant ionic strength. Recently, thermodynamics of exchange of hydrated transition metal ions in ammonium mordenite was studied by Barrer[9]. The ion exchange characteristics of tantalum arsenate are of considerable interest because of the possible use of this material as a cation exchanger and its application for the separation of rare earth ions[10]. Kinetic studies on the exchange of Ag^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Y^{3+} and Th^{4+} ions with hydrogen ion on tantalum arsenate have been reported[11]. The ion exchange was found to be particle diffusion controlled and depend upon the hydrated radii of the ingoing cations.

The present report concerns the influence of temperature on the equilibria of Mg^{2+}-H^{+}, Ca^{2+}-H^{+}, Sr^{2+}-H^{+}, Ba^{2+}-H^{+}, La^{3+}-H^{+} and Th^{4+}-H^{+} with respect to tantalum arsenate at constant ionic strength within the temperature range from 20 to 50°.

Experimental

Reagents : Tantalum pentoxide (BARC, India) and sodium arsenate (Riedel, Germany) were used. All other reagents used were of AnalaR grade.

22.10 g of tantalum pentoxide was heated with 200 g of ammonium sulphate in 200 ml of concentrated sulphuric acid. The clear solution was diluted to 500 ml to obtain a solution which was 0.1*N* with respect to tantalum. Sodium arsenate (0.1*N*) solution was prepared in 2*N* hydrochloric acid.

Tantalum arsenate, synthesized as reported in our earlier work[10,11] was sieved to 50-100 mesh and washed free from fine particles. The hydrogen form of the exchanger was prepared with 2*N* nitric acid and was converted to the respective metal ion forms by placing the exchanger in 0.1*N* solutions of the metal chlorides or nitrates for 24 hrs with intermittent replacement of the solution. All samples were washed free of chloride ions, air dried and equilibrated to constant weight in an atmosphere of 51% humidity.

The water contents of the various samples of the exchanger was determined by heating to constant weight in an air oven at 200°. The exchange capacities were found by eluting with 2*N* hydrochloric acid in a column and analysing the effluent for alkaline earth metal ions, with EDTA, using Eriochrome black T as indicator, and lanthanum and thorium, using xylenol orange as indicator.

Equilibration experiments : In the equilibration experiments, 0.2 g samples of the hydrogen form of the exchanger were shaken at the desired temperature in an electric SICO shaker for 6 hrs with 20 ml of a solution containing hydrochloric acid or nitric acid, the appropriate alkaline earth metal chloride, and lanthanum and thorium nitrates at a total ionic strength of 0.1*N*. Experiment showed that equilibrium was attained within this period and the supernatant solution was analysed for the metal ions. The experiments were conducted at 20, 30, 40 and 50° with ±1° variation.

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Reversibility test : Before equilibrium thermodynamic procedures could be applied to any experimental isotherm data, it was necessary to establish that true equilibrium conditions existed over the whole isotherm. Thus isotherm points were measured in the reverse direction also, starting with the metal exchanged form of the tantalum arsenate. The term "reversible" as used in this paper means that true equilibrium conditions were found to exist over the whole isotherm, that is, the forward and reverse isotherms coincided within experimental uncertainty.

Reversibility test was made by the conventional method of equilibrating known weights of tantalum arsenate maximally exchanged by the magnesium ion with isotherm solution in the manner described in the previous section.

Results and Discussion

Capacity and water content measurements : The ion exchange capacity and water content values for magnesium, calcium, strontium, barium, lanthanum and thorium forms of the exchanger are given in Table 1. It can be seen that the capacity for the

TABLE 1 —WATER CONTENT AND ION EXCHANGE CAPACITY OF SOME METAL IONS ON TANTALUM ARSENATE

Metal ion	Water Content (%)	Ion Exchange Capacity of Cationic form of Exchanger (meq/g)	Ion Exchange Capacity of Hydrogen form of Exchanger (meq/g)
Mg^{2+}	17.20	0.82	0.98
Ca^{2+}	14.47	0.88	1.09
Sr^{2+}	10.18	0.92	1.14
Ba^{2+}	10.13	0.97	1.21
La^{3+}	10.36	0.68	0.92
Th^{4+}	11.18	0.52	0.78

alkaline earth metal chloride solution increases in the order $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$. Similar variations of the capacity of zirconium phosphate with the nature of the ingoing cation have been observed by other workers[14,15]. The values of ion exchange capacity and water content indicate that the metals enter the matrix as hydrated ions and the marked difference in the capacity can be accounted for the differences in the number of associated water dipoles. Sites close to the hydrated metal ions may thus be effectively blocked for the exchange reaction. In addition to the above factors it is well known that tantalum arsenate exhibits ion-sieve properties resulting in an uptake which would be governed by the relative sizes of the hydrated alkaline earth ions in agreement with the observed order of capacities. Analogous behaviour was found by other workers[14] on zirconium phosphate.

Ion-exchange isotherms : The study of different cations and reversibility test for the exchange reaction Mg^{2+}-H^+ indicate that the exchange is reversible under the experimental error range. The selectivity coefficient for the reaction

$$n\bar{R}H^+ + M^{n+} \rightleftharpoons \bar{R}_nM + nH^+ \qquad \ldots (1)$$

is defined by

$$S = \frac{\bar{X}_M}{X_M} \cdot \frac{(X_H)^n}{(\bar{X}_H)^n} \qquad \ldots (2)$$

where $\bar{X}_M$ and $\bar{X}_H$ refer to the equivalent fractions of the metal and hydrogen ions in the exchanger and X_M and X_H, the equivalent fraction of the metal and hydrogen ions in the solution.

The thermodynamic equilibrium constant for the reaction (1) may be written in terms of activity coefficients, f,

$$K_H^M = \frac{\bar{X}_M \cdot \bar{f}_M \, (X_H)^n \, (f_H)^n}{X_M \, f_M \, (\bar{X}_H)^n \, (\bar{f}_H)^n}$$

$$= S \cdot \frac{\bar{f}_M \cdot (f_H)^n}{f_M \, (\bar{f}_H)^n} \qquad \ldots (3)$$

The ratio of activity coefficients in the solution, f_H/f_M can be calculated from the mean ionic activity coefficients of pure salt solutions at same ionic strength of 0.1*N* by the method due to Glueckauf[15], since these dilute solutions will not deviate greatly from ionic strength principle at 20° to 50°, neglect of the temperature dependence of the activity coefficients ratio will not be serious deviation in the values of K_H^M especially for ion exchange reactions[5,16,17], therefore the thermodynamic equilibrium constant is obtained as

$$K_H^M = S \cdot \frac{\bar{f}_M}{(\bar{f}_H)^n} \qquad \ldots (4)$$

The solid phase activity coefficients are given by[18]

$$\ln \bar{f}_M = -(1-\bar{X}_M) \ln S + \int_{\bar{X}_M}^{1} \ln S \, d\bar{X}_M \qquad \ldots (5)$$

and

$$\ln \bar{f}_H = \bar{X}_M \ln S - \int_{0}^{\bar{X}_M} \ln S \, d\bar{X}_M \qquad \ldots (6)$$

By numerical integration of log S against $\bar{X}_M$ curves using the above relationships, the solid phase activity coefficients and the thermodynamic equilibrium constants given in Tables 2 and 3 were calculated for the exchange of hydrogen ion with Mg, Ca, Sr, Ba, La and Th ions.

TABLE 2—SELECTIVITY COEFFICIENTS AND SOLID PHASE ACTIVITY COEFFICIENTS FOR Mg^{2+}-H EXCHANGE AT 20±1°C

X_{Mg}	$\bar{X}_{Mg}$	S_H^{Mg}	$\bar{f}_{Mg}$	$\bar{f}_H$	K_H^{Mg}
0.025	0.022	0.8919	0.44	1.02	0.377
0.050	0.038	0.7444	0.52	1.01	0.379
0.102	0.062	0.5610	0.67	0.99	0.378
0.150	0.084	0.4831	0.76	0.97	0.388
0.212	0.121	0.4616	0.79	0.96	0.395
0.253	0.144	0.4345	0.81	0.94	0.398
0.325	0.214	0.4849	0.79	0.97	0.389
0.389	0.267	0.4888	0.78	0.98	0.397
0.454	0.288	0.3716	0.85	0.90	0.399
0.537	0.302	0.2479	0.90	0.75	0.396
0.612	0.322	0.1714	0.95	0.64	0.397
0.755	0.348	0.0652	1.21	0.44	0.407

Mean K = 0.391

TABLE 3—MEAN THERMODYNAMIC EQUILIBRIUM CONSTANT (K_H^M) VALUES AT DIFFERENT TEMPERATURES

Exchange	K_H^M (mean)	Exchange	K_H^M (mean)
At 20±1°C		*At 30±1°C*	
Mg^{2+}-H^+	0.391	Mg^{2+}-H^+	0.453
Ca^{2+}-H^+	0.471	Ca^{2+}-H^+	0.695
Sr^{2+}-H^+	0.557	Sr^{2+}-H^+	0 625
Ba^{2+}-H^+	0.893	Ba^{2+}-H^+	1.070
La^{3+}-H^+	0.553	La^{3+}-H^+	0.692
Th^{4+}-H^+	0.159	Th^{4+}-H^+	0.275
At 40±1°C		*At 50±1°C*	
Mg^{2+}-H^+	0.555	Mg^{2+}-H^+	0.623
Ca^{2+}-H^+	0.835	Ca^{2+}-H^+	0.950
Sr^{2+}-H^+	0.732	Sr^{2+}-H^+	0.787
Ba^{2+}-H^+	1.358	Ba^{2+}-H^+	1.537
La^{3+}-H^+	0.892	La^{3+}-H^+	1 102
Th^{4+}-H^+	0.311	Th^{4+}-H^+	0.493

The free energy changes, ΔG° for the ion exchange were calculated from the thermodynamic equilibrium constants using the general relation

$$\Delta G^\circ = -\frac{RT}{Z_H \cdot Z_M} \ln K_H^M \quad (7)$$

where R is the gas constant, Z_H, Z_M are the valence of competing ionic species, T is the absolute temperature. The free energy changes, ΔG° are given in Table 4.

TABLE 4—THERMODYNAMIC PROPERTIES FOR THE EXCHANGE OF METAL IONS WITH HYDROGEN ION ON TANTALUM ARSENATE AT 20±1°C

Displacing Ion	ΔG° (Cal mole^{-1})	ΔH° (Cal mole^{-1})	ΔS° (Cal deg^{-1} mole^{-1})	ΔS_{EX} (Cal deg^{-1} mole^{-1})
Mg^{2+}	276	−1941	− 5.1	−36.7
Ca^{2+}	220	−1454	− 5.7	−17.1
Sr^{2+}	171	−1105	− 4.3	−11.6
Ba^{2+}	83	−1666	− 5.8	− 3.5
La^{3+}	116	−1579	− 5.8	−49.8
Th^{4+}	270	−2727	−10.2	—

The ΔH° values are calculated from the plot of $\log_{10}K$ against 1/T. The ΔH° values for the exchange of the alkaline earth metals and hydrogen ion show that heat was evolved. In general ΔH° appeared to be a function of the difference of the hydration of the exchanging cations and was small for ions of similar hydration number and large for ions of widely differing hydration number.

The entropy changes, ΔS° corresponding to the ion exchange process were calculated using the equation

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad \ldots (8)$$

The calculated ΔS° values are given in Table 4. The entropy differences between the corresponding ionic forms of the exchanger, ΔS_{EX} can be written[19]

$$\Delta S^\circ = \Delta S_{EX} - (S_M^\circ - S_H^\circ) \quad \ldots (9)$$

where S° = the aqueous ionic entropies[20]. Values of ΔS_{EX} are included in Table 4 and reflect (i) changes in hydration accompanying reaction (1) and (ii) the differences in lattice distortion of the two forms of the exchanger. The ΔS_{EX} values in Table 4 show a significant increase with the size of the ingoin cation. The observed order Mg<Ca<Sr<Ba is consistent with the proposed increasing hydration of the alkaline earth metal ions within the exchanger. It is seen that this trend becomes apparent only after removing the variable $(S_M^\circ - S_H^\circ)$ term from the measured ΔS°. The change in entropy, ΔS° show no correlation with the hydrated ionic radius but increases slightly in magnitude as a linear functions of the bare ion radius. On this basis, the exchange is envisaged as occurring between the covalently bound hydrogen and hydrated cations in the interstitial liquid, the affinity being inversely proportional to the degree of hydration during exchange the polarized hydration shell is displaced and the liberated hydrogen ion become hydrated. The net change in entropy equals that due to the replacement of one cation by another plus the entropy difference between the hydrated forms of the two ions involved, and the overall value of ΔS° is thus less for very large hydrated ions. Sr^{2+} ion does not follow the general trend probably due to the hydrolysis of the Sr^{2+} in neutral solutions ($Sr^{2+} + H_2O \rightarrow SrOH^+ + H^+$).

Acknowledgement

The authors thank Prof. W. Rahman for research facilities. Thanks are also due to the Council of Scientific and Industrial Research (India) for the financial assistance to Pritam Singh Thind.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 823-825

Studies on North Gangetic Deposits from Farraka (Bengal) to Mansi (Bihar) in India

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Manuscript received 20 May 1978, revised 2 May 1980, accepted 27 May 1980

Twenty-three samples from North Gangetic belt starting from Farraka (Bengal) to Mansi (Bihar) in India have been analytically studied. The percentage composition of the constituents along with pH, swelling index, loss on ignition, bulk density etc. have been reported. The cation exchange capacity values have been found to vary from 4.45 to 18.42 m.e per 100 g. The water holding capacities determined at different temperatures (26° to 75°) have been recorded. The important observation that log of water holding capacity plotted against the inverse of absolute temperature results in the straight line, has been reported ; this type of observation is not available in the literature with other soil samples studied.

THE properties and chemical behaviours of some different river deposits have been studied[1-6]. North Gangetic river belt is not a permanent belt and whenever the course of river changes the old soil deposits from various points mixing in very very dilute aqueous medium are carried to some other points as new deposits. The study of these deposits appears to have not been done in order to throw light on the characteristics of regular and irregular deposits by the river Ganges. In addition to the chemical and physical properties of the soil samples of a particular region we have undertaken to study the water holding capacity at different temperatures.

Experimental

Twenty-three soil samples collected from 0-20 cm depth from different places from northern Gangetic belt starting from Farraka (Bengal) to Mansi (Bihar) in summer of 1975 before flood by BNS and MMP were taken for investigations. The samples were dried in air oven for a few hours and then powdered to pass through 150 mesh sieve (0.104 mm). The powder samples were dried at 110°-120° for 24 hours. The dried powder was kept in a closed desiccator and used for all determinations. These samples were analysed for definite chemico-physical properties following standard methods[7,8]. The average percentage deviation in the determination of percentage of SiO_2, Al_2O_3 and Fe_2O_3 was found to be ±1.52 per cent, ±0.65 per cent and ±0.45 per cent respectively obtained from these determinations.

The C.E.C. values were obtained by treatment with standard K_2CO_3 solution following volumetric measurements against standard hydrochloric acid solution[9]. These values with *p*H, swelling index, bulk density, loss on ignition and water holding capacity at $26\pm1°$ were obtained and recorded in Table 1. The deviation in cation exchange capacity in m.e per 100 g never exceeded ±0.46.

The water holding capacity of the soils were obtained at different temperatures (26 to 75°) and are recorded in Table 2. The log of water holding capacity is plotted against the inverse of absolute temperature and the straight lines obtained are shown in Fig. 1.

Results and Discussion

The percentage of SiO_2 in these samples is very high (74 to 84.65 p.c.) as is expected with the soil samples of these belts. It is interesting to note that the percentage of Al_2O_3 varying from 5.00 to 12.80 is nearly twice the percentage of Fe_2O_3 varying from 2.32 to 6·86 at both ends of the limit covering a big length from Farraka to Mansi (Vide Table 1). In almost all cases the percentage of carbon is more than the percentage of nitrogen resulting in the high value of C/N ratio to 31·20. The total percentage of phosphorous in these samples is very poor and in out of 23 samples studied nine gave just the qualitative positive test showing its presence in traces only.

Some of the soil samples of this belt are alkaline and some of them are acidic with a limit of *p*H from 8.1 to 6.5 further showing that these samples are neither strongly alkaline nor strongly acidic in character. The cation exchange capacity determined from standard K_2CO_3 solution varies from 4.45 to 18.42 m.e per 100 g. It is clear from these data

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that the cation exchange capacity of these soils is predominantly due to bivalent exchangeable cations, calcium ion (0.12 to 1.62 p.c.) has been reported to occur in the soil samples but no definite relation between the amount of bivalent cation and the C.E.C. values could be established, may be due to heterogeneous character of the soil samples of this belt. The p.c. of alkali oxide has been found to vary from 0.06 percent to 0.32 p.c. in most of the cases except for sample no. 23,3 and 16 for which the values are respectively 0.62 p.c., 0.54 p.c. and 0.42 p.c. The swelling index of these samples does not vary much and the loss on ignition which includes the loss of the combined water and decomposable substances ranges from 5.25 to 8.60 p.c. The bulk density which is a measure of porosity at a particular temperature varies from 1.04 to 1.32.

TABLE 1—PHYSICO-CHEMICAL CHARACTERISTICS OF THE SOIL SAMPLES

Sl. No.[x]	Al_2O_3 p.c.	Fe_2O_3 p.c.	pH	C.E.C. m.e/100 g	Capacity water holding at 26°
1	2	3	4	5	6
1.	6.32	4.86	6.50	10.52	40.25
2.	7.25	3.42	7.20	12.56	40.00
3.	12.44	6.86	6.60	18.42	55.25
4.	8.20	5.20	7.80	15.24	44.26
5.	10.85	5.00	7.50	10.20	25.98
6.	12.80	6.12	6.70	4.867	54.20
7.	8.02	4.02	7.10	8.60	60.25
8.	7.52	3.45	7.60	7.72	35.38
9.	12.22	6.68	8.00	15.52	36.42
10.	10.42	4.12	8.10	10.25	49.25
11.	8.62	3.82	7.20	8.26	52.50
12.	7.25	3.18	6.70	12.75	29.75
13.	7.25	3.02	7.40	4.85	26.00
14.	9.25	4.84	6.60	15.25	18.25
15.	5.25	3.86	7.20	10.20	39.45
16.	5.00	3.42	6.90	8.25	32.26
17.	11.46	3.50	7.70	12.26	16.35
18.	9.36	5.21	7.70	4.45	48.60
19.	9.00	3.10	6.60	5.37	42.95
20.	7.54	4.00	4.90	6.25	35.68
21.	7.12	2.32	7.80	9.12	31.75
22.	11.22	4.25	6.80	6.45	28.25
23.	9.30	3.84	6.90	12.68	42.65

x. Name of the places from where the samples were collected: 1. Khajuria Ghat (Farraka North), 2 Manickchak (Maldah-W.B.), 3. Maharajpur diara (S.P.-Bihar), 4. Amdabad, 5. Naulakha, 6. Manihari diara (Katihar-Bihar), 7. Shobhanpur diara (S.P.-Bihar), 8. Bari Kodarjana diara (North), 9 Karhagola Ghat (Katihar-Bihar), 10 Tintanga, 11. Saidpur diara, 12. Mahadeopur Ghat, 13. Chawania, 14. Lattipur diara, 15. Chakfatma, 16. Gangapur diara (Bhagalpur-Bihar), 17. Korchakka-Bharat Khand, 18. Salarpur, 19. Agwani, 20. Thuthi Sirajpur, 21. Sriniya diara, 22. Gogri diara, 23. Mansi (Monghyr).

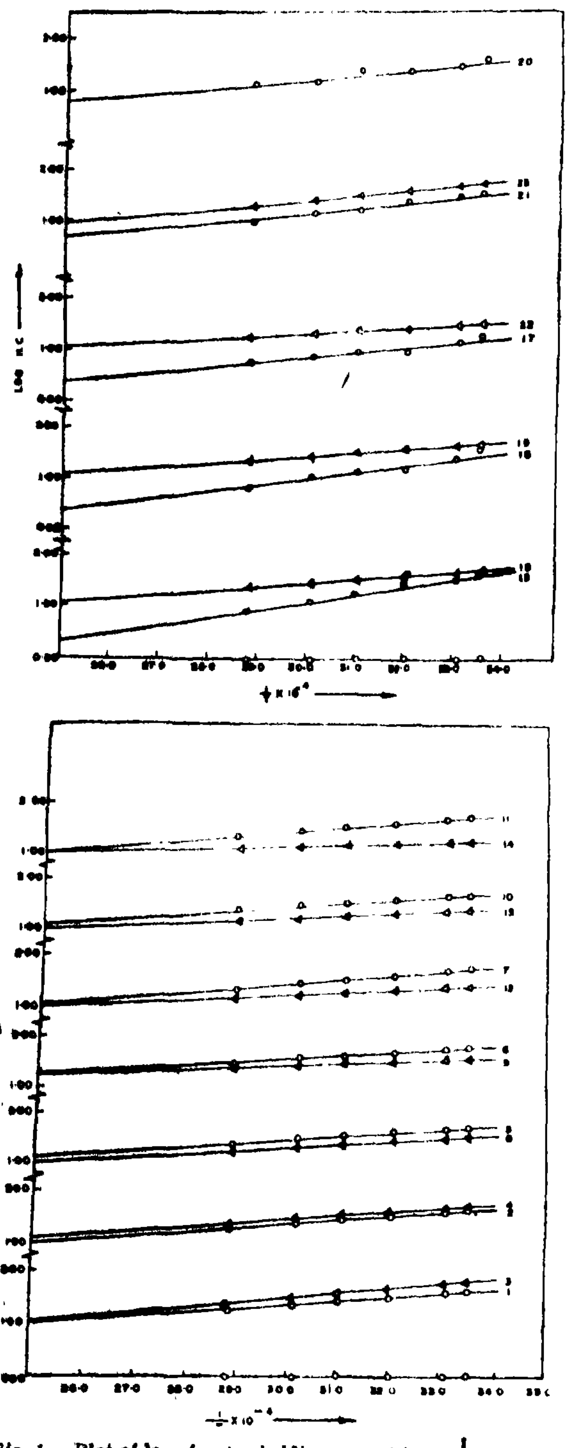


Fig. 1. Plot of log of water holding capacities vs $\frac{1}{T}$

The water holding capacity of these soils have been determined at different temperatures from 26° to 75°. With rise in temperature the values for water holding capacity have been found to decrease. Above 75° these values have been found to be erratic and meaningless. It has been tried to plot log of water holding capacity (H.C) against the inverse of absolute temperature when straight line is obtained (vide Fig. 1). It is an important observation with the soils of this belt that the

straight line relation in between log H.C and $\frac{1}{T}$ holds good. It is interesting to note that the values of antilog of Y at $\frac{1}{T}=25\times10^{-4}$ deg^{-1} comes out to be equal to the percentage of $Fe_2O_3+Al_2O_3$ obtained experimentally. The comparative values are tabulated in Table 2. In majority of the cases the results are well comparable and in few cases wide variation noticeable may be due to structural differences. The water holding capacity of soil might depend on the composition of the soil and on increasing the temperature the texture of the soil may change resulting in the decrease of the water holding capacity. It is proposed that such physico-chemical studies of the deposits of river Ganges at regular intervals of time may reveal the nature of the chemical composition of the deposits when soluble and insoluble constituents in very dilute aqueous medium are carried from one place to other during erosion.

TABLE 2—PERCENTAGE OF $Fe_2O_3+Al_2O_3$ FROM THE STRAIGHT LINE AT $\frac{1}{T}=25\times10^{-4}$ deg^{-1} (VIDE FIGURE 1)

Sl. No.	p.c. of $Fe_2O_3+Al_2O_3$ from Table 1	p.c. of $Fe_2O_3+Al_2O_3$ from straight line at $\frac{1}{T}=25\times10^{-4}$ deg^{-1}
1	2	3
1.	11.18	10.00
2.	10.67	10.96
3.	19.30	10.00
4.	13.40	13.18
5.	15.85	14.79
6.	18.92	17.78
7.	12.04	12.59
8.	10.97	11.22
9	18.90	15.84
10.	14.54	14.12
11.	12.44	11.22
12.	10.43	10.47
13.	10.54	11.22
14.	14.09	10.00
15.	9.11	2.63
16.	8.42	2.51
17.	14.96	2.40
18.	14.57	14.12
19.	12.10	12.59
20.	11.54	6.31
21.	9.44	4.47
22.	15.47	11.22
23.	13.14	8.91

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 826-828

Synthesis of New 3-Aminoacetyl Carbamide-4-Thiazolidones and Their Fungicidal Properties

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Manuscript received 3 August 1979, revised 25 March 1980, accepted 12 June 1980

Various 3-aminoacetyl carbamide-4-thiazolidones(IV) were synthesized by the reaction of mercaptoacetic acid with arylidene-1-(hydrazoacetyl)-3-substituted carbamides(III).

THIAZOLIDONE derivatives exhibit a variety of pharmacological activities[1-4]. The presence of N−C−S linkages has been postulated to account for the antifungal activity of 4-thiazolidones[5]. Attempts have been made earlier to enhance the fungitoxicity of thiazolidone derivatives by introducing different substituents either at 2, 3 or 5 position in the thiazolidone ring[6-10].

These observations prompted the synthesis of various 3-aminoacetyl carbamide-4-thiazolidones (Fig. 1) in order to ascertain the effect of substituted acetyl carbamides attached to the 3-position of the 4-thiazolidones on fungitoxicity. 1-(Hydrazoacetyl-3-substituted carbamides(II) were obtained by the reaction of hydrazine hydrate with chloroacetylcarbamides(I). Condensation of (II) with aromatic aldehydes in glacial acetic acid furnished arylidene-1-(hydrazoacetyl)-3-substituted carbamides(III), and the structure of these compounds was established by their analytical data and i.r spectral data which showed absorption bands at 3200-3300 cm^{-1} (N−H stretching), 1610-1665 cm^{-1} (CONH, C=N), 1490-1540 cm^{-1} (C−N stretching) and 750-875 cm^{-1} (monosubstituted benzene). Reaction of (III) with mercaptoacetic acid in dry dioxan yielded 3-aminoacetyl carbamide-4-thiazolidones(IV). The i.r. spectra of these compounds showed bands at 1650-1685 cm^{-1} (ring C=O), 1600-1610 cm^{-1} (CONH, C=C aromatic), 1420-1520 cm^{-1} (C−N stretching), 1250-1310 cm^{-1} (C−S−C) and 745-820 cm^{-1} (substituted benzene).

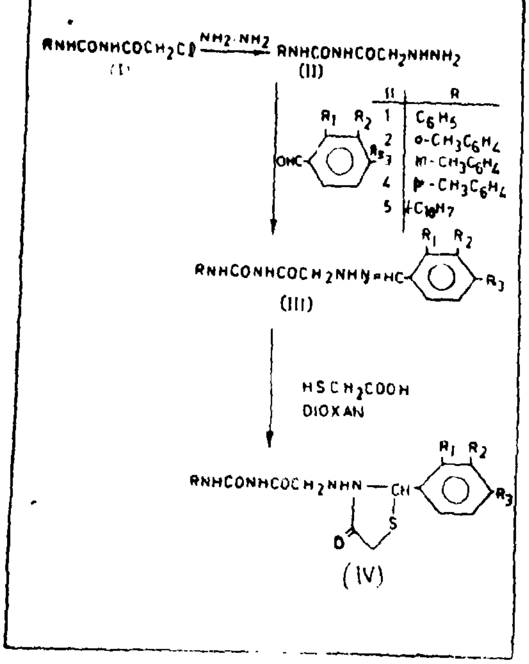


Fig. 1

Experimental

Infrared spectra was obtained in KBr pallets on Perkin-Elmer infrared spectrophotometer. Melting points are uncorrected.

Chloroacetyl carbamides(I) were synthesised by the methods reported earlier[11-14].

1-Hydrazoacetyl-3-substituted carbamides(II_{1-6}).

Hydrazine hydrate 99% (0.15 mole) was added to the solution of appropriate chloroacetyl carbamides (I, 0.15 mole) in absolute ethanol and the resulting mixture was heated under reflux for 6-8 hrs. A solid separating from the refluxing solution was filtered off after the solution had cooled and crystallized from ethanol to yield **II** (R=C_6H_5) − m.p. 149-50°, yield 60%. (Found : C, 51.82 ; H, 5.03 ; N, 26.73%. Calcd. for $C_9H_{12}N_4O_2$: C, 51.92 ; H, 5.77 ; N, 26.92%). **II** (R=o−$CH_3C_6H_4$) − m.p. 171-72°, yield 58%, (Found : C, 54.32 ; H, 6.08 ; N, 25.25%. Calcd. for $C_{10}H_{14}N_4O_2$: C, 54.05 ; H, 6.30 ; N, 25.22%). **II** (R=m-$CH_3C_6H_4$) − m.p., 280-82° ; yield 50%, (Found : C, 54.29 ; H, 6.05 ; N, 25.38%. Calcd. for $C_{10}H_{14}N_4O_2$; C, 54.05 ; H.

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6.31 ; N, 25.22%), II ($R=p\text{-}CH_3C_6H_4$) – m. p., 165 ; yield, 65%, (Found : C, 54.00 ; H, 6.70 ; N, 25.00%, Calcd. for $C_{10}H_{14}N_4O_2$: C, 54.05 ; H, 6.31 ; N, 25.22%) and II ($R=\alpha\text{-}C_{10}H_7$) – m.p., 149-51° ; yield, 50%, (Found : C, 60.06 ; H, 5.33 ; N, 21.44%. Calcd. for $C_{13}H_{14}N_4O_2$: C, 60.46 ; H, 5.81 ; N, 21.74%).

Arylidene-1-(hydrazoacetyl)-3-substituted carbamides(III) :

A mixture of (II, 0.01 mole) and a suitable aldehyde (0.01 mole) in glacial acetic acid was refluxed for 5-6 hrs. The reaction mixture was cooled, poured into ice cold water and the product, which precipitated out was collected by filtration, washed several times with water and then crystallised from ethanol and ethanol-water. Compounds synthesized are recorded in Table 1. All the compounds showed consistent elemental analyses.

TABLE 1— ARYLIDENE-1-(HYDRAZOACETYL)-3-SUBSTITUTED CARBAMIDES(III)

Compd.* No	R_1	R_2	R_3	M.P. °C
	$R=C_6H_5$			
1.	H	H	H	100-01
2.	H	H	CH_3	93-5
3.	OH	H	H	200-01
4.	H	H	NO_2	141-2
5.	H	OCH_3	OH	120
	$R=o\text{-}CH_3C_6H_4$			
6.	H	H	H	127-28
7.	H	H	CH_3	85-87
8.	OH	H	H	77-78
9.	H	H	NO_2	121
10.	H	OCH_3	OH	87
	$R=m\text{-}CH_3C_6H_4$			
11.	H	H	H	105-6
12.	H	H	CH_3	117
13.	H	H	NO_2	139-40
14.	H	OCH_3	OH	131-32
	$R=p\text{-}CH_3C_6H_4$			
15.	H	H	H	111-12
16.	H	H	CH_3	122
17.	OH	H	H	85
18.	H	H	NO_2	228
19.	H	OCH_3	OH	220
	$R=\alpha\text{-}C_{10}H_7$			
20.	H	H	H	195-7
21.	H	H	CH_3	185
22.	OH	H	H	121
23.	H	H	NO_2	194
24.	H	OCH_3	OH	191-2

* yields varied between 55-70%.

3-Aminoacetyl carbamide-4-thiazolidones(IV) :

Mercaptoacetic acid (0.015 mole) was added to a well stirred solution of (III, 0.05 mole) in 50 ml dry diozan. The mixture was refluxed for 3-4 hrs. The excess of solvent was removed under reduced pressure. On cooling, the solid mass which separated out was washed with 10% sodium bicarbonate solution and finally recrystallised from the proper solvent. The melting points and analytical data of these compounds are recorded in Table 2. All the compounds showed consistent elemental analyses.

TABLE 2—3-AMINOACETYL CARBAMIDE-4-THIAZOLIDONES(IV)

Compd.* No.	R_1	R_2	R_3	Solvent of crystallization	M.P. °C
	$R=C_6H_5$				
1.	H	H	H	a	182-83
2.	H	H	CH_3	b	152
3.	OH	H	H	c	154-56
4.	H	H	NO_2	b	122
5	H	OCH_3	OH	a	145-46
	$R=o\text{-}CH_3C_6H_4$				
6.	H	H	H	b	280d
7.	H	H	CH_3	a	180
8.	OH	H	H	a	153-54
9.	H	H	NO_2	b	202-3
10	H	OCH_3	OH	b	168
	$R=m\text{-}CH_3C_6H_4$				
11.	H	H	H	c	181-82
12.	H	H	CH_3	b	163
13.	H	H	NO_2	c	135
14.	H	OCH_3	OH	b	136
	$R=p\text{-}CH_3C_6H_4$				
15.	H	H	H	b	136-37
16.	H	H	CH_3	a	238
17.	OH	H	H	c	125
18.	H	H	NO_2	c	235-36
19.	H	OCH_3	OH	a	250
	$R=\alpha\text{-}C_{10}H_7$				
20.	H	H	H	c	165-66
21.	H	H	CH_3	c	200
22.	OH	H	H	c	170
23.	H	H	NO_2	c	209-10
24.	H	OCH_3	OH	a	202-3

* Yields ranged between 40-65%. a, Alcohol-water , b. Alcohol , c. Dioxan.

Fungicidal activity :

The compounds recorded in Table 2 were screened for their antifungal activity against *Helminthosporium oryzae* and *Fusarium equiseti* at concentrations 2 and 0.2% (W/V) by Paper-disc plate method[15]. None of the compounds exhibited significant antifungal activity against any of the test fungi at any of the test concentrations.

Acknowledgement

The authors are thankful to Dr. D. S. Bhakuni, CDRI, Lucknow for i. r. and microanalysis of the compounds.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 829-832

Synthesis of Alkyl/Arylaminopropionyl-2-Amino-4-Phenyl Thiazole, 2-Aminobenzothiazole and 2-Amino (Substituted)Benzothiazole as Potential Local Anaesthetics

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Manuscript received 29 August 1979, revised 28 March 1980, accepted 27 May 1980

Various alkyl/arylaminopropionyl derivatives of 2-amino-4-phenylthiazole, 2-aminobenzothiazole and 2-amino (substituted) benzothiazoles were prepared by treating each of the 2-amino-4-phenylthiazole, 2-aminobenzothiazole and 2-amino (substituted) benzothiazoles with β-chloropropionyl chloride whereby β-chloropropionyl derivatives of 2-amino-4-phenylthiazole, 2-aminobenzothiazole and 2-amino(substituted)benzothiazoles were obtained. These were subsequently treated with various amines to afford dimethylaminopropionyl-, diethylaminopropionyl-, dipropylaminopropionyl-, diisopropylaminopropionyl-, morpholinopropionyl-, piperidinopropionyl-, piperizinopropionyl-, N-ethylanilinopropionyl-, pyridine-2-aminopropionyl-, and pyrimidine-2-aminopropionyl-2-amino-4-phenylthiazole, -2-aminobenzothiazole and -2-amino(substituted)benzothiazoles. Almost all the compounds were tested for their local anaesthetic activity and most of them have shown considerable activity.

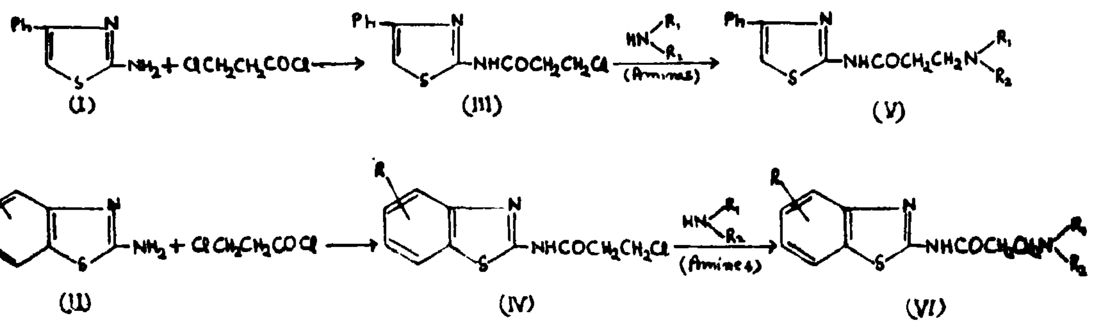
IT has been found that alkyl/arylaminoacetyl derivatives of 2-amino-4-phenylthiazole[1], 2-aminobenzothiazole[2,3], 2-amino (substituted) benzothiazoles[4-6] and 2-phenylamino-4-phenylthiazole[7] have shown considerable local anaesthetic activity. It was thought worthwhile to synthesise various alkyl/arylaminopropionyl derivatives of 2-amino-4-phenylthiazole, 2-aminobenzothiazole and 2-amino(substituted)benzothiazoles as potential local anaesthetics. These compounds were prepared by treating 2-amino-4-phenylthiazole(I), 2-aminobenzothiazole and 2-amino(substituted)benzothiazoles(II) with β-chloropropionyl chloride whereby β-chloropropionyl derivatives (III & IV) of 2-amino-4-phenylthiazole, 2-aminobenzothiazole and 2-amino(substituted)-benzothiazoles were obtained. These were subsequently treated with various amines to afford various alkyl/arylaminopropionyl-2-amino-4-phenylthiazole(V), 2-aminobenzothiazole and 2-amino-(substituted) benzothiazoles(VI).

The sequence of reactions may be depicted as :

Different amines used in condensation with III & IV were dimethylamine, diethylamine, dipropylamine, diisopropylamine, morpholine, piperidine, piperizine, N-ethylaniline, 2-aminopyridine and 2-aminopyrimidine.

The compounds (V & VI) prepared were characterised on the basis of their elemental analysis and ir spectra. The ir spectra of these compounds showed characteristic absorption peaks in the region of 1650-1600 cm^{-1} and 1360-1320 cm^{-1} corresponding to C=O group and C–N bond respectively. Absorption band in the region of 3230-3160 cm^{-1} indicated –NH– stretching frequency. Absorption peak in the region of 1720-1670 cm^{-1} showed the lactam (–C(=O)–N) band.

The ir spectra were carried on Perkin-Elmer spectrophotometer. The m.p.s of the compounds



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TABLE—CONDENSATION OF 2-AMINO-4-PHENYLTHIAZOLE, 2-AMINOBENZOTHIAZOLE AND 2-AMINO(SUBSTITUTED)BENZOTHIAZOLE WITH β-CHLOROPROPIONYL CHLORIDE : FORMATION OF β-CHLOROPROPIONYL DERIVATIVES OF 2-AMINO-4-PHENYLTHIAZOLE 2-AMINOBENZOTHIAZOLE AND 2-AMINO(SUBSTITUTED) BENZOTHIAZOLES



Sl. No.	Nature of R	Nature of R′	Molecular Formula	Yield %	M.P. °C		Analysis N	Analysis S
1.	Phenyl	—	$C_{12}H_{11}N_2OSCl$	59	176-177	Found	10.25	12.34
						Calc.	10.50	12.00
2.	—	H	$C_{10}H_9N_2OSCl$	60	192	Found	11.26	13.65
						Calc.	11.64	13.30
3.	—	4-Methyl	$C_{11}H_{11}N_2OSCl$	58	173	Found	11.39	12.18
						Calc	11.00	12.57
4.	—	6-Methyl	$C_{11}H_{11}N_2OSCl$	[illegible]	181	Found	10.61	11.96
						Calc.	11.00	12.57
5.	—	6-Ethoxy	$C_{12}H_{13}N_2O_2SCl$	57	210	Found	10.23	11.61
						Calc.	9.84	11.24

were determined on Toshniwal melting point apparatus. The elemental analyses of the compounds were carried at C.D.R.I., Lucknow and University of Roorkee, Roorkee and are found to be consistent with the respective molecular formula. Local anaesthetic activity of these compounds was tested in the Division of Pharmacology and Toxicology, Indian Veterinary Research Institute, Izatnagar.

Experimental

β-Chloropropionyl-2-amino-4-phenylthiazole :

Freshly distilled β-chloropropionyl chloride (3.8 g) in dry benzene (10 ml) was gradually added to 2-amino-4-phenylthiazole[8] (5.2 g) dissolved in dry benzene (35 ml) containing triethylamine (3 ml), with constant shaking. When the addition was complete, the reaction mixture was refluxed on a water bath for 2 hr. Benzene was distilled off and the residue was washed with sodium bicarbonate and water to remove the acid impurities. The product was finally washed with water and crystallised from ethanol, yield 59%, m. p. 176-177. Found : N, 10.25% ; S, 12.34% ; Calcd for $C_{12}H_{11}N_2OSCl$; N, 10.50 ; S, 12.00%.

Similarly β-chloropropionyl derivatives of 2-aminobenzothiazole[9] and 2-amino (substituted)-benzothiazole[9] were prepared and are summarised in the above Table.

Condensation of β-chloropropionyl derivatives of 2-amino-4-phenylthiazole, 2-aminobenzothiazole and 2-amino(substituted)benzothiazole with various amines : Formation of alkyl/arylaminopropionyl-2-amino-4-phenylthiazole, 2-aminobenzothiazole and 2-amino-(substituted)benzothiazoles.

Diethylaminopropionyl-2-amino-4-phenylthiazole :

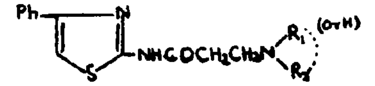
To β-chloropropionyl-2-amino-4-phenylthiazole (2.6 g) dissolved in ethanol (20 ml), diethylamine (3 ml) was added gradually. When the addition was complete, reaction mixture was refluxed for 6 hr. After the reaction, excess of ethanol and diethylamine were recovered by distillation. The residue was washed with sodium bicarbonate to remove the acid impurities and finally with water. The product was crystallised from ethanol, yield 62%, m.p. 108. Found : C, 62.71 ; N, 13.61 ; S, 10.38% ; Calcd for $C_{16}H_{21}N_3OS$; C, 63.36 ; N, 13.86 ; S, 10.56%.

Similarly dimethylaminopropionyl-, dipropylaminopropionyl-, diisopropylaminopropionyl-, morpholinopropionyl-, piperidinopropionyl-, piperizinopropionyl-, N-ethylanilinopropionyl-, pyridine-2-aminopropionyl-, pyrimidine-2-aminopropionyl derivatives of 2-amino-4-phenylthiazole, 2-aminobenzothiazoles and 2-amino(substituted)benzothiazoles were prepared by condensing β-chloro propionyl derivatives of 2-amino-4-phenylthiazole, 2-aminobenzothiazole and 2-amino(substituted)benzothiazole with corresponding amines and are summarised in Tables 1-5.

The bases so obtained were converted to their hydrochloride by passing dry HCl gas into their ethereal solutions.

The picrates of these bases were prepared by treating the base with picric acid in benzene.

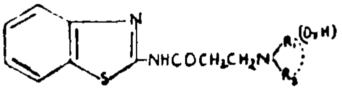
TABLE 1—CONDENSATION OF β-CHLOROPROPIONYL-2-AMINO-4-PHENYLTHIAZOLE WITH VARIOUS AMINES : FORMATION OF VARIOUS ALKYL/ARYLAMINOPROPIONYL-2-AMINO-4-PHENYLTHIAZOLES



Sl. No.	Nature of R_1 (or H) / R_2	Yield %	M.P. °C	Melting points of hydrochlorides °C	Melting points of picrates °C
1.	Dimethyl	58	103	169-170	182-183
2.	Diethyl	62	108	173-174	189-190
3.	Dipropyl	60	92-93	155	197-198
4.	Diisopropyl	57	110-112	141-142	175-176
5.	Morpholino	62	118-119	189-190	188
6.	Piperidino	59	104	161-162	178-180
7.	Piperizino	61	114-115	153-154	155-156
8.	N-ethylanilino	60	136-137	120-122	192-193
9.	Pyridine-2	62	145	185-186	204
10.	Pyrimidine-2	59	110-111	135	170

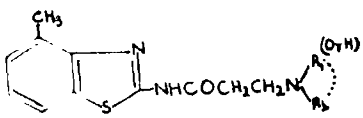
* Elemental analysis of all the compounds were consistent with the respective molecular composition.

TABLE 2—CONDENSATION OF β-CHLOROPROPIONYL-2-AMINOBENZOTHIAZOLE WITH VARIOUS AMINES : FORMATION OF VARIOUS ALKYL/ARYLAMINOPROPIONYL-2-AMINOBENZOTHIAZOLE



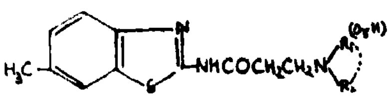
Sl. No.	Nature of R_1 (or H) / R_2	Yield %	M.P. °C	Melting points of hydrochlorides °C	Melting points of picrates °C
1.	Diethyl	60	52	105-106	238
2.	Dipropyl	63	57-58	111-112	247
3.	Diisopropyl	59	—	96-97	193-194
4.	Morpholino	61	—	103-104	225-226
5.	Piperidino	58	—	89-90	249-250
6.	Piperizino	60	—	99	230-231
7.	Diphenyl	62	92-93	123-124	240-241
8.	N-ethylanilino	57	145-146	139	244-245
9.	Pyridine-2-	59	111	127-128	251-252
10.	Pyrimidine-2-	56	84-85	135-136	257-258

TABLE 3—CONDENSATION OF β-CHLOROPROPIONYL-2-AMINO-4-METHYLBENZOTHIAZOLE WITH VARIOUS AMINES : FORMATION OF VARIOUS ALKYL/ARYLAMINOPROPIONYL-2-AMINO-4-METHYLBENZOTHIAZOLE



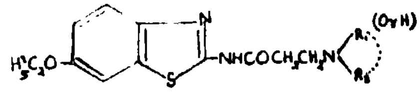
Sl. No.	Nature of R_1 (or H) / R_2	Yield %	M.P. °C	Melting points of hydrochlorides °C	Melting points of picrates °C
1.	Dimethyl	58	71-72	112-113	159-160
2.	Diethyl	60	84-85	125	188-190
3.	Dipropyl	61	80-81	139-140	114
4.	Diisopropyl	58	105-106	151-152	162-163
5.	Morpholino	60	92-93	146-147	203
6.	Piperidino	57	87	109-110	185
7.	Piperizino	61	113-114	142-143	176-178
8.	N-ethylanilino	56	77	187-188	212-213
9.	Pyridine-2-	58	132-133	221-222	250-251
10.	Pyrimidine-2-	54	D	151-152	143-144

TABLE 4—CONDENSATION OF β-CHLOROPROPIONYL-2-AMINO-6-METHYLBENZOTHIAZOLE WITH VARIOUS AMINES : FORMATION OF VARIOUS ALKYL/ARYLAMINOPROPIONYL-2-AMINO-6-METHYLBENZOTHIAZOLES



Sl. No.	Nature of R_1 (or H) / R_2	Yield %	M.P. °C	Melting points of hydrochlorides °C	Melting points of picrates °C
1.	Dimethyl	57	90	123	205-206
2.	Diethyl	59	95-96	149-150	259-260
3.	Dipropyl	61	106-107	168-169	250-251
4.	Diisopropyl	56	112	160	D
5.	Morpholino	62	134	175-176	197-198
6.	Piperidino	60	102-103	165-166	D
7.	Piperizino	59	D	179	218
8.	N-ethylanilino	57	192-193	153-154	184-185
9.	Pyridine-2-	60	77-78	180-181	243-244
10.	Pyrimidine	56	90-92	199-200	266

TABLE 5—CONDENSATION OF β-CHLOROPROPIONYL-2-AMINO-6-ETHOXYBENZOTHIAZOLE WITH VARIOUS AMINES : FORMATION OF VARIOUS ALKYL/ARYLAMINOPROPIONYL-2-AMINO-6-ETHOXYBENZOTHIAZOLES



Sl. No.	Nature of R_1 (or H) / R_2	Yield %	M.P. °C	Melting points of hydrochlorides °C	Melting points of picrates °C
1.	Dimethyl	57	96	175	194-195
2.	Diethyl	59	137-138	203-204	241-242
3.	Dipropyl	60	141-142	193-194	D
4.	Diisopropyl	58	D	187-188	230-231
5.	Morpholino	62	101-102	172-173	212
6.	Piperidino	60	119	208-209	234
7.	Piperizino	63	156-157	210-211	219-220
8.	N-ethylanilino	59	135-136	—	D
9.	Pyridine-2-	57	179	215-216	235-236
10.	Pyrimidine-2-	56	169-170	195	219-220

Biological Activity :

Almost all the compounds mentioned in Tables 1-5 were tested for their local anaesthetic activity (surface anaesthetic[10,11] and infiltration anaesthetic activities[12]). The compounds were tested as their hydrochlorides and most of them have shown considerable local anaesthetic activity. The activity results of these compounds were compared with standard local anaesthetic xylocaine HCl and some of them were found to have longer anaesthetic action than xylocaine.

Acknowledgement

The authors are thankful to Dr. M. S. Mehra, Principal, Bareilly College, Bareilly, Shri K. G. Kamthan for providing necessary laboratory facilities and to Shri S. N. Mehra and Shri T. L. Arora

(Camphor and Allied Product, Bareilly, U.P.) for carrying out I. R. spectra of compounds. The authors are also thankful to the Director, Indian Veterinary Research Institute, Izatnagar, Bareilly for providing facilities in the Division of Pharmacology and Toxicology for getting the compounds screened.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 833-834

Aza Triterpenes II+ : A-Aza Triterpenes of the Lactones of Methyl Oleanonate and Methyl Betulonate

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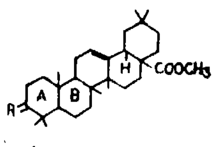
Manuscript received 8 June 1979, revised 28 April 1980, accepted 21 May 1980

Schmidt reaction of methyl oleanonate(I), methyl betulonate(II) with PPA and Beckmann rearrangement of their oximes (IA & IIA) with PPA gave a complex mixture. Treatment of the oximes (IA & IIA) with conc. sulphuric acid-glacial acetic acid mixture gave the lactams (IIIB & IVB) and the seconitriles (IIIC and IVC). Beckmann rearrangement of the ketolactone oximes (IIIA & IVA) with $POCl_3$-pyridine gave lactams (IIIB & IVB) and seconitriles (IIIC & IVC). Schmidt reaction of ketolactones (III & IV) gave the lactams (IIIB & IVB).

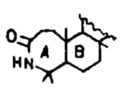
WE had earlier reported[1] the Schmidt reaction of methyl oleanonate, methyl betulonate and lupenone and Beckmann rearrangement of their oximes. It had been reported in the literature[2] that PPA was a superior reagent in the Schmidt reaction and Beckmann rearrangement. PPA acts both as a solvent and a reagent.

In the present investigation, Schmidt reaction of methyl oleanonate(I), methyl betulonate(II) and Beckmann rearrangement of their oximes (IA & IIA) with PPA gave a dark brown semi solid. TLC examination of this product indicated it to be a complex mixture, the constituents of which could not be separated by the usual chromatographic techniques (column and preparative).

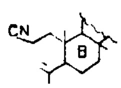
Under strong acidic conditions, the pentacyclic triterpene carboxylic acids and their methyl esters of olean group[3] are known to lactonise and lupane group lactonise with expansion of ring E[4]. It is therefore expected even in the present case, since PPA being a strong acid besides Schmidt reaction and Beckmann rearrangement, lactonization also might had taken place leading to the formation of the normal, lactams (IB/IIB) and 3, 4 seconitriles



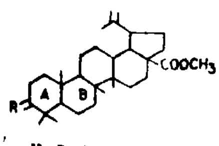
I R=O
IA R=N-OH



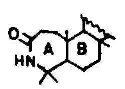
I B



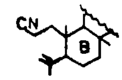
I C



II R=O
IIA R=N-OH



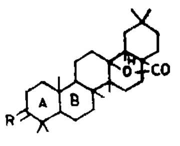
II B



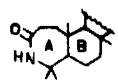
II C

(IC/IIC), lactams of lactones (IIIB/IVB) and nitriles of the lactones (IIIC/IVC) besides other products which could not be isolated and identified.

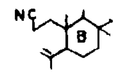
Since sulphuric acid is also a strong acid, Beckmann rearrangement of the oximes (IA/IIA) were conducted with sulphuric acid-acetic acid mixture (1 : 1). The reaction yielded lactams of lactones (IIIB & IVB) [IR 1665 cm^{-1} the seven membered lactam carbonyl : 1760 cm^{-1} γ-lactone carbonyl : 3220 cm^{-1} –NH and the 3, 4 seconitriles of the lactones (IIIC & IVC) IR 1760 cm^{-1} γ-lactone carbonyl : 2220 cm^{-1} –CN].



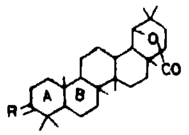
III R=O
IIIA R=N-OH



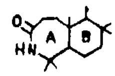
III B



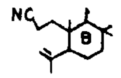
III C



IV R=O
IVA R=N-OH



IV B



IV C

The lactone lactams (IIIB & IVB) and 3, 4 seconitriles of lactones (IIIC & IVC) were prepared by the Beckmann rearrangement $POCl_3$-pyridine 30-35°) of the 3-keto oximes (IIIA & IVA) of the lactones (III & IV). The lactones(III & IV) were prepared by treatment of the corresponding 3-ketones (I & II) with glacial acetic acid-sulphuric acid mixture (1 : 1) [IR 1700 cm^{-1} six membered carbonyl : 1760 cm^{-1} lactone carbonyl].

Schmidt reaction of the ketolactones (III & IV) (NaN_3-benzene containing a few drops of conc. sulphuric acid) gave lactams (IIIB & IVB).

* Part of the work presented at the Annual Convention of Chemists, 1977 at Jaipur.

Experimental

Melting points are uncorrected. IR spectra were recorded on Perkin-Elmer spectrophotometer in chloroform. All the compounds showed consistent elemental analysis.

Beckmann rearrangement of the Oximes (IA & IIA) with PPA :

A typical experiment is described.

A mixture of oxime (700 mg) and PPA (30 g) was heated with stirring at 120-130° for 30 mts. The reaction mixture was poured into crushed ice, neutralised with 50% NaOH and extracted with ether (5 × 100 ml). Removal of the solvent after drying over anhydrous magnesium sulphate, yielded a dark brown semi-solid (500 mg). It did not separate into distinct spots on TLC with various solvent systems indicating complex nature of the product.

Schmidt reaction of the Ketones(I & II) with PPA :

A typical experiment is described.

NaN_3 (0.68 g) was added with slow stirring to a mixture of 1 g of the ketone and 50 g of PPA at 50-60°. The temperature was maintained for 10 hrs. The reaction mixture was poured into crushed ice, made alkaline with 50% NaOH and extracted with ether (5 × 100 ml). Removal of the solvent after drying over anhydrous magnesium sulphate gave a dark brown semi-solid similar to that obtained in Beckmann rearrangement.

Beckmann rearrangement of the Oximes(IIIA & IVA) :

A typical experiment is described.

The oxime (1 g) was dissolved in pyridine (30 ml freshly distilled over KOH) and $POCl_3$ (1 ml) was added drop by drop cooling the reaction mixture in ice. After the addition of $POCl_3$ the reaction mixture was kept at 30-35° for 4 hours ; poured into ice-cold water, extracted with ether and the pyridine was removed by washing the ether extract with dilute hydrochloric acid. The residue obtained on removal of the solvent was adsorbed over alumina column and eluted with benzene and chloroform. Benzene eluate gave the 3, 4 seconitriles. The seconitriles (IIIC & IVC) crystallise from methanol and acetone as colourless needles, (yield 100 mg) chloroform eluate gave the lactam. The lactams (IIIB & IVB) crystallise from methanol or chloroform as colourless needles (yield 300 mg).

Action of Glacial acetic acid-conc. Sulphuric acid mixture on Oximes (IA & IIA) : Isolation of lactone lactams (IIIB & IVB) and 3, 4 seconitriles (IIIC & IVC) :

A typical experiment is described.

The oxime (2.5 g) was dissolved in glacial acetic acid-conc. sulphuric acid mixture (100 ml, 1 : 1) and kept at room temperature overnight. The reaction mixture on dilution with ice-cold water gave a colourless mass. This was adsorbed over alumina column and eluted with benzene and chloroform. Benzene eluate gave lactone lactams. The lactone lactams crystallise from methanol as colourless needles and the chloroform eluate gave 3, 4 seconitriles. The 3, 4 seconitriles crystallise from methanol as colourless needles, and had m.p.s (IIIC, 245° and IVC 242°).

Schmidt reaction of the Ketolactones(III & IV) :

NaN_3 (0.5 g) was added with slow agitation during the course of 1 hour to a solution of the ketone (1 g in 40 ml of benzene containing 4 ml of concentrated sulphuric acid) at 60-65°. The temperature was maintained for 10 hrs and the reaction mixture was poured into crushed ice, made alkaline with 5% NaOH and extracted with ether (5 × 100 ml). Removal of the solvent gave the lactam (550 mg). The lactams crystallise from acetone or methanol as colourless needles and had m.p.s (IIIB, above 280° and IVB, above 280°)

Acknowledgement

The authors are grateful to Prof. M. L. N Reddy, Principal and Head, Department of Chemistry, Nizam College, Hyderabad for providing facilities. SKR thanks U.G.C. for financial support. KLR and SKR are grateful to V. V. Research Centre, Hyderabad for encouragement.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 835-836

Synthesis of Some New 2-Aryl-3-Hetaryl-4(3H) Quinazolones

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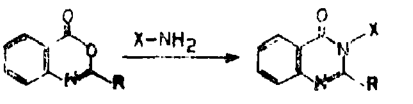
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Manuscript received 27 June 1979, revised 21 February 1980, accepted 18 May 1980

2-Aryl (alkyl)-benzoxazin-4-ones (I, R = CH_3, C_6H_5, $C_6H_5CH_2$, p-$NO_2C_6H_4$) are condensed with 2-amino hetaryls (pyridyl, pyrimidyl, thiazolyl), 1 & 2-amino anthraquinones, p-amino acetophenone and 1,2-diamines like ethylene diamine and o-phenylene diamine. The products are obtained in excellent yields and are characterised by infrared and elemental analysis.

THE quinazolone chemistry with its diverse biological properties like CNS depressant[1,2], anticonvulsant[3,4], muscle relaxant[5,6], and antiviral[7] has got much importance in recent years. The structural modification at the 3-aryl moiety has shown excellent results in pharmacology. The present work aims at synthesizing a number of quinazolone derivatives supposed to be potentially active.

The reported[8] literature procedure was followed for the synthesis of quinazolones and all the products were characterised by infrared and elemental analysis. In all the benzoxazinones the carbonyl of the lactone ring gave a peak around 1680 cm^{-1}. In contrast, when the benzoxazinones react with amines, the nitrogen inserted products showed intense peak at 1650-1660 cm^{-1} region indicating the presence of an amide carbonyl. As a part of our programme to synthesize some new heterocyclics with a bridgehead nitrogen atom particularly at the 3,4-positions, the benzoxazinones were allowed to react with simple 1,2-diamines like o-phenylene diamine and ethylene diamine. To our surprise it was observed that out of the two

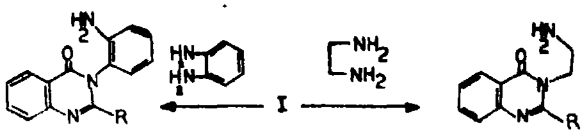


I II-IX

a = R = CH_3, b = R = C_6H_5 c = R = $C_6H_5CH_2$; d = R = p-$NO_2C_6H_4$
X = II, 2-Pyridyl, III, 2-Pyrimidyl,
IV, 2-Thiazolyl; V, p-carboxyphenyl,
VI, p-methyl carboxyphenyl (p-$C_6H_4CH_2COOH$),
VII, p-acetophenyl, VIII, 1-anthraquinonyl,
IX, 2-anthraquinonyl;

Scheme 1

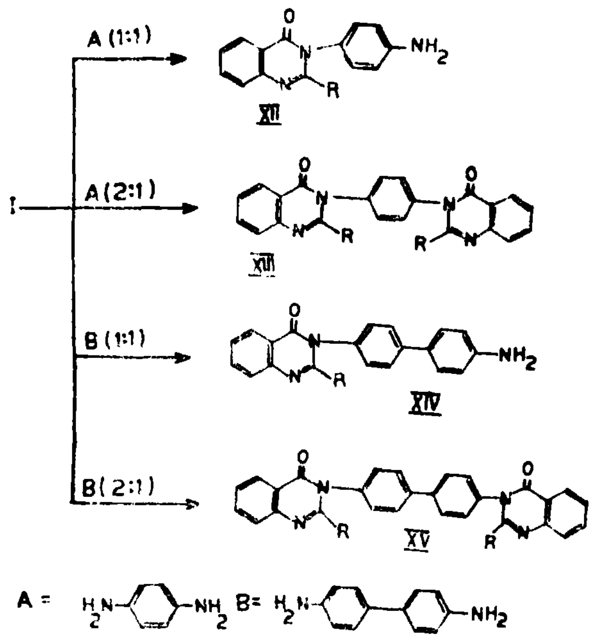
available amino groups, only one takes part in the insertion. This finding was supported by the positive test for amino group (azo dye test in case of o-phenylene diamine) and the appearance of a peak at 3350 cm^{-1} (NH stretching) in system X and XI (Scheme 2). Construction of a five membered ring is precluded probably due to steric reasoning. In contrast however, systems like p-phenylene diamine,



XI X

Scheme 2

benzidine where both the amino functions are far apart gave products of the type XII and XIV. Additionally when two molar quantities of the benzoxazinones were taken and allowed to react with one molar quantity of the amines, the structure of the products dramatically changed to XIII and XV (Scheme 3). These observations led us to infer that nitrogen atoms of both the amino functions were taken up in the insertion processes.



Scheme 3

Further, the benzoxazinones on reaction with amines like 1-aminoanthraquinone, 2-aminoanthraquinone and *p*-amino acetophenone gave crystalline coloured products.

Experimental

All melting points were taken in open capillaries and are uncorrected. The IR spectra were recorded on a Perkin-Elmer 137 spectrophotometer. TLC were run over silica gel plates.

Preparation of 2-R-benzoxazinones :

Acetyl anthranil I ($R=CH_3$) was prepared following the procedure available in literature[9], m.p. 79-80° (lit,[9] 80-81°). The other 2-R-benzoxazinones I ($R=C_6H_5$, $C_6H_5CH_2$ and p-$NO_2C_6H_4$) were prepared following literature procedure[8]. I, $R=C_6H_5$, m.p. 121° (lit[10], m.p. 123°), yield 80% ; $R=C_6H_5CH_2$, m.p. 165°, 83% ; $R=p$-$NO_2C_6H_4$, m.p. 200° (lit.[10], m.p. 203°), 78%.

Reaction of 2-R-benzoxazinones with amines—General Procedure :

Equimolar (0.01 mol) mixture of 2-R-benzoxazinone and the amine was taken in pyridine (20 ml) and the solution was heated under reflux for 6 hr. Then the reaction mixture was cooled to room temperature, poured into ice water and neutralised with conc. HCl when the solid product separated out. The solid was filtered, washed with cold water several times and dried. The crude product was crystallised from alcohol or alcohol-water mixture. Only in two cases of 1,4-diamines (*p*-phenylene diamine and benzidine) the benzoxazinone and the amine were taken in 2 : 1 molar ratios to obtain the products X and XII respectively following the usual procedure. All the compounds were obtained in high yields (50-80%) and gave satisfactory C, H and N analysis. Compound II a, b, c and d had melting points 176°, 113°, 178° and 232° respectively. Compound III a, b, c and d had m.ps 170°, 155°, 183° and 220° ; Compound IV a, b, c and d had m.ps 178°, 218°, 179° and 200° ; Compound V a, b, c and d had m.ps 261-63°, 159-60°, 168° and 190° ; Compound VI a, b, c and d had m.ps 253°, 161°, 145° and 189° ; Compound VII a, b, c and d had m.ps 245°, 110°, 165-67° and 185° ; Compound VIII a, b, c and d had m.ps 262°, 185° and 190° ; Compound IX a, b, c and d had m.ps 162-63°, 136-37°, 180° and 201° ; Compound X a, b, c and d had m.ps 170°, 239°, 175° and 201° ; Compound XI a, b, c and d had m.ps 180°, 85°, 186° and 135°, Compound XII a, b, c and d had m.ps 161°, 186°, 160° and 103° ; Compound XIII a, b, c and d had m.ps 167°, 166°, 175° and 115° ; Compound XIV a, b, c and d had m.ps 275, 255°, 239° and 205° and Compound XV a, b, c and d had m.ps 215°, 241°, 168° and 220° respectively.

Acknowledgement

The authors are thankful to Prof. P. S. Radhakrishna Murti, Head of the Dept. of Chemistry, Berhampur University, for laboratory facilities and to U.G.C., New Delhi for financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 837-840

Synthesis and Antifertility Activity of 5-Oxo-5 H-Benzofuro (6, 5-C)[2] Benzopyran and Its Basic Ether Derivatives

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Manuscript received 30 November 1979, accepted 21 May 1980

Synthesis and anti-implantation activity of some 9,10-diphenyl-5-oxo-5H-benzofuro (6, 5-c) [2] benzopyran and its 10-(p-alkylamino alkoxy)-phenyl derivatives are reported. The compounds have been characterized by IR, NMR and elemental analysis. Considerable anti-implantation activity is observed in a few compounds.

IT is well known that furocoumarins[1] possess remarkable pharmacological properties. Tetrahydro Cannabinol[2], a dibenzo-(b, d)-pyran derivative possesses psychomimetic activity. Psoralen[3], the well known furocoumarin prevents pregnancy in rats probably due to its estrogenic activity. In an attempt to obtain an "artificial" substitute for the scarce steroidal hormones, Dodd's[4] group was able to find out the estrogenic activity of phenanthrone derivative ; the first synthetic non-steroidal compound to be recorded. Chawla *et al*[5] have shown that 2,3-diphenyl benzofurans possess significant anti-implantation activity. The same authors in an attempt to study the structure-activity relationship synthesized a number of related compounds. Amongst this group of compounds 2-phenyl-3-[*p*-(*β*-pyrrolidinoethoxy)-phenyl]-naphtho (2, 1-b) furan[6], a higher homolog of 2,3-diphenyl benzofuran was found to be the most active.

Several furocoumarins (linear and angular) containing *bis* cyclic triarylethylene systems[7], a cyclic triarylethylene system carrying simultaneously either stilbene[8] or stilbesterol[9] moieties in a rigid cyclic system were studied. Encouraged by the results it seemed of interest to study the effect of new furocoumarins (9,10-diphenyl-5-oxo-5H-benzofuro (6,5-c) [2] benzopyran) incorporating a phenanthrone like 6-oxo-6H-dibenzo (b, d) pyran and furan moiety with a cyclic triarylethylene system, on the fertility control.

Hydroxy coumarins needed as starting materials were synthesized by the Hurtley's[10] procedure reviewed recently by Devlin[11]. Under these conditions, with orcinol two products were obtained and they were easily separated by column chromatography, however the yield of other isomer (5-hydroxy-3,4-benzocoumarin) is about 0.4% of the total crude products. Hydroxy coumarins (2',4'-dihydroxy-biphenyl-2-carboxylic acid lactones) were then condensed with desyl chloride/4-methoxyphenyl-α-chloro-benzyl ketone to get the respective desyl ethers. They were cyclized to give linear furocoumarin by the method reported earlier[12]. The methoxy furocoumarin was demethylated using pyridine hydrochloride. The hydroxy compound obtained was condensed with hydrochlorides of various alkylaminoalkoxy/propoxychloride hydrochlorides.

5,7-Dihydroxy-3, 4-benzocoumarin (1 mole) obtained by the reaction of phloroglucinol with *o*-bromo benzoic acid was condensed with (0.5 mol) of desyl chloride and the monodesyl ether obtained, was methylated first to have a smooth alkali cyclization.

The IR spectra of furocoumarins and their predecessors, coumarinyl-*O*-desyl ethers were studied. In case of furocoumarins absorption is observed around 1700 (lactone carbonyl), 1500-1600 (strong absorption of C=C stretching) and 1500-1400 attributable to –C–O–C stretch of furan, and 800-900 assignable to furan ring breathing. In case of desyl-ethers in addition to bands at 1700, 1500-1600, peaks around 1200-1300 (attributable to ether bridge) and 1680 cm^{-1} (acyl carbonyl) were also observed.

Anti-implantation activity :

The *in vivo* anti-implantation activity of basic ether derivatives (IVa-i) were studied in adult albino rats at the Regional Research Laboratory, Jammu Tawi. In this preliminary screening female rats were treated with the drug at a dose of 10 mg/kg. The compounds were suspended in a mixture of gum acacia and distilled water. The suspension was fed orally from days 1-7 *post coitum*. The day on which the vaginal smears showed the presence of spermatozoa was considered as the day one of pregnancy. The animals were Laparotomized on day 10 of pregnancy and the number of implantation sites were recorded.

Mean number of implantation sites were calculated by adding the implantation sites in pregnant rats

and dividing them by the total number of rats treated—pregnant as well as non-pregnant. Only 80-83% inhibition of implantation was observed with few compounds at this dose level. Details are given in Table I. Among the basic ether derivatives, pyrrolidino and N, N-diethylamino groups are more active, whereas the higher homolog (piperidino propyloxy) was found to be more effective than its lower homolog 'piperidino ethyloxy derivative'.

TABLE 1

Compound IV	Dose mg/kg i.p. (No. of animals)	% inhibition of implantation	Mean No. of implantation	% mortality during first 10 days
a	10(5)	0	9.6 ±0.68	Nil
b	10(6)	0	9.6 ±1.12	Nil
c	10(5)	0	9.4 ±0.6	Nil
d	10(5)	50	4.25±2.65	20
e	10(6)	33.3	6.66±2.6	Nil
f	10(6)	33.3	4.3 ±3.84	50
g	10(6)	33.3	6.0 ±1.91	Nil
h	10(6)	83.3	1.4 ±1.16	Nil
i	10(6)	80.0	1.8 ±0.84	20

Experimental

The IR spectra were measured on Perkin-Elmer 577 and NMR on XL-100 MHz and EM. 390.90 MHz spectrometer using TMS as an internal reference.

2',4'-Dihydroxy-biphenyl-2-carboxylic acid lactones. I (7-Hydroxy-3,4-benzocoumarin).

A solution of 2-bromo benzoic acid (0.05 mol), hydroxy benzene (0.1 mol) and sodium hydroxide (0.1 mol) in water (30 ml) were heated under reflux for 30 min. A 10% aq. solution of copper sulphate (5 ml) was then added, and the mixture was heated under reflux for an additional 10 min. It was then cooled, filtered, washed well with water and dried. This material was of sufficient purity to be used as such for further preparations. The following compounds were obtained by the above route are :

Ia : 7-Hydroxy-3,4-benzocoumarin, m.p. 230-34°.

Ib : 7-Hydroxy-8-methyl-3,4-benzocoumarin, m.p. 258-60°.

Ic : 5,7-Dihydroxy-3,4-benzocoumarin, m.p. 294-302° (d).

2',4'-Dihydroxy-6'-methyl-biphenyl-2-carboxylic acid lactone : (7-Hydroxy-5-methyl-3,4-benzocoumarin) Id :

This compound was prepared by the copper catalysed condensation of *o*-bromo benzoic acid (4.43 g ; 0.022 mol) and orcinol (5.0 gm, 0.040 mol) in aq. 1.5*N* sodium hydroxide solution (27 ml) in the general number described above, with the exception that the reaction mixture was heated under reflux for 1 hr following the addition of copper sulphate solution. The crude product (1.68 gm, 33%) was crystallized from glacial acetic acid to provide (1.47 g). m.p. 159-62°.

Desyl ether preparation : II

The hydroxy coumarin (0.011 mol) was refluxed with desylchloride (0.01 mol) in dry acetone and potassium carbonate media for 24 hrs. The inorganic salts were filtered off, the solvent was distilled off, crude compound was obtained when treated with 1% sodium hydroxide. Crystallized the crude product from dioxane. Obtained this way are

IIa : 7-*O*-Desyl-3,4-benzocoumarin, m.p. 180-81°.

IIb : 7-*O*-Desyl-8-methyl-3,4-benzocoumarin, m.p. 218-20°.

IIc : 7-*O*-Desyl-5-methyl-3,4-benzocoumarin. m.p. 220-25°.

NMR (DMSO-d_6)

3.2 – three proton singlet of 5 methyl.
6.6 – one proton singlet methine proton of side chain.
8.15 – one proton singlet of 8H.
7.4-7.9 – fifteen proton multiplet aromatic protons.

IId : 5,7-Dihydroxy-3,4-benzocoumarin (2.50 gm ; 0.011 mol) was refluxed with desylchloride (2.305 gm ; 0.01 mol) and worked up as usual to get the monodesylether, m.p. 225-28°.

IIe : The compound IId (4.22 gm ; 0.01 mol) and dimethyl sulfate (0.63 gm ; 0.005 mol) in acetone-pot. carbonate medium were refluxed for 24 hrs and worked up as usual to get the 7-*O*-desyl-5-methoxy-3,4-benzocoumarin crystallized from dioxane, m.p. 168-73°.

IIf : 7-Hydroxy-3,4-benzocoumarin Ia (2.343 gm ; 0.01 mol) was also condensed with 4-methoxyphenyl-α-chlorobenzylketone (2.60 gm ; 0.01 mol) in lieu of desylchloride. On working up it gave 7-(1'-phenyl-2'-*p*-methoxy-phenyl-2'-oxo)-ethyloxy-3,4-benzocoumarin crystallized from ethanol, m.p. 169-70°.

Cyclization : III

Desylether (1 mol) was dissolved in minimum amount of dioxane and 0.1*N* aq. potassium hydroxide (3 mol) added and refluxed for 6-8 hrs. Filtered, clear filtrate was neutralized with dil. HCl to get the furocoumarin. The furocoumarins obtained this way were crystallized from dioxane.

IIIa : 9,10-diphenyl-5-oxo-5H-benzofuro (6,5-c) [2] benzopyran from (IIa), m.p. 200-202°.

IIIb : 7-methyl-9,10-diphenyl-5-oxo-5H-benzofuro (6,5-c) [2] benzopyran from (IIb), m.p. 248-50°.

IIIc : 11-methyl-9, 10-diphenyl-5-oxo-5H-benzofuro (6,5-c) [2] benzopyran from (IIc), m.p. 265-70°.

IIId : 11-methoxy-9, 10-diphenyl-5-oxo-5H-benzofuro (6,5-c) [2] benzopyran from (IIe), m.p. 215-17°.

IIIe : 9-phenyl-10-(*p*-methoxyphenyl)-5-oxo-5H-benzofuro (6,5-c) [2] benzopyran from (IIf), m.p. 230-32.

NMR [IIIA] :

3.7-three proton singlet, methoxyl.

8.1-one proton singlet 7H.

7.1-one proton singlet 11H.

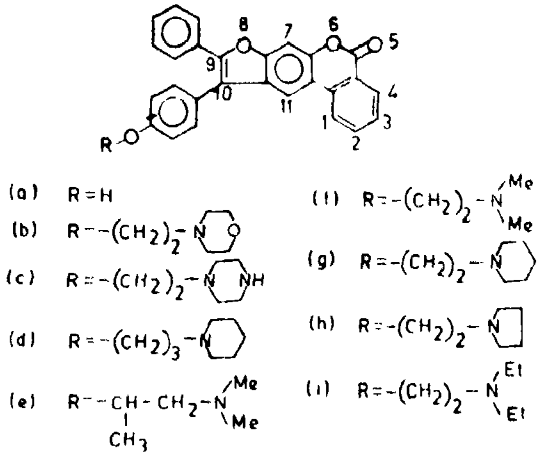
7.3-7.5-thirteen proton multiplet. Aromatic protons (two side phenyl H's.+H's. of 1,2,3,4-position).

Demethylation : IV

The compound (IIIe) (3.94 g ; 0.01 mol) was heated with distilled pyridine hydrochloride (11.5 g ; 0.10 mol) at 230-40° for ½ hr and then mixed with water. The product on crystallization with dioxane gave 9-phenyl-10-(*p*-hydroxyphenyl)-5-oxo-5H-benzofuro (6, 5-c) [2] benzopyran(IV), m.p. 288-90°.

The compound(IV) (0.01 mol) was mixed with hydrochlorides of the various bases (0.011 mol) ; acetone (500 ml) and anhydrous potassium carbonate (6 gm) and the mixture was refluxed for 24 hrs. On working up the reaction mixture as usual, a solid separated that was crystallized from appropriate solvent (Table 2).

TABLE 2—BASIC ETHER DERIVATIVES OF 10-(p-HYDROXY PHENYL)-9-PHENYL-5-OXO-5H-BENZO FURO (6,5-C) [2] BENZOPYRAN



Compound	Molecular formula	m.p. °C	Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
a	$C_{23}H_{14}O_4$	288-90	78.95	4.21	—	77.9	4.25	—
b	$C_{29}H_{27}O_5N$	120-21	76.59	5.22	2.71	75.8	5.1	2.8
c	$C_{31}H_{29}O_4N_2$.*HCl	279-81 (d)	75.6	5.69	5.69	74.9	5.6	5.7
d	$C_{35}H_{31}O_4N$	150-52	78.9	5.99	2.71	78.7	5.83	2.7
e	$C_{32}H_{27}O_4N$	108-10	77.42	5.81	3.01	77.45	5.8	2.95
f	$C_{29}H_{25}O_4N$	160-63	77.16	5.54	3.10	77.1	5.49	3.0
g	$C_{33}H_{29}O_4N$	155-58	78.21	5.91	2.85	79.00	5.85	2.79
h	$C_{34}H_{29}O_4N$	135-39	79.2	5.63	2.72	79.0	5.59	2.7
i	$C_{33}H_{29}O_4N$	150-53	77.6	6.05	2.92	77.0	6.0	2.89

All the melting points are uncorrected.
* Separated as salt. (Hydrochloride).

Acknowledgement

The authors wish to thank Prof. K. Koteswara Rao, Principal, Regional Engineering College, Warangal for providing facilities. One of the authors (BVR) is grateful to the CSIR, New Delhi for the award of a junior research fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 841-843

Synthesis of Quinolino Oxazoles as Optical Brighteners

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Manuscript received 21 August 1979, accepted 12 June 1980

A few 2-aryl and 2-heterocyclic substituted quinolino (3 : 4) oxazoles have been synthesized by condensing the substituted 3-amino-4-hydroxy quinoline with aromatic and heterocyclic carboxylic acids employing polyphosphoric acid as cyclodehydrating agent. The U.V., I.R., mass and fluorescence spectra of some of these compounds have been presented for characterization.

PYRIDINE and quinoline derivatives are good optical brighteners exhibiting blue fluorescence and these are also stable to hypochlorite[1]. 2-Amino-3-cyano-7-(dimethylamino)-quinoline and its derivatives show an intense blue fluorescence in day light and brighten synthetic fibres[2]. 7-Hydroxy-3-benzoxazolo quinoline was reported to be strongly fluorescent[3]. In view of the established fluorescent properties of 3-oxazolo quinoline derivatives it was thought interesting to synthesize quinoline (3 : 4) oxazoles to investigate their optical brightening properties.

Earlier 2-aryl quinolino (3 : 4) oxazoles were prepared by heating the 3-amino-4-hydroxy quinoline with respective aromatic acid anhydrides in moderate yields[4].

In the present investigation, polyphosphoric acid is used as cyclodehydrating agent for the synthesis of quinolino (3 : 4) oxazoles. For the purpose of synthesizing the title compounds—2-methyl-3-amino-4-hydroxy quinoline and 2, 8-dimethyl-3-amino-4-hydroxy quinoline were condensed with aryl and substituted coumarin-3-carboxylic acids and terephthalic acid to get the corresponding 2-substituted quinolino (3 : 4) oxazoles.

The 3-amino-4-hydroxy quinolines are prepared following the procedure reported earlier[5] improving

Chart - I

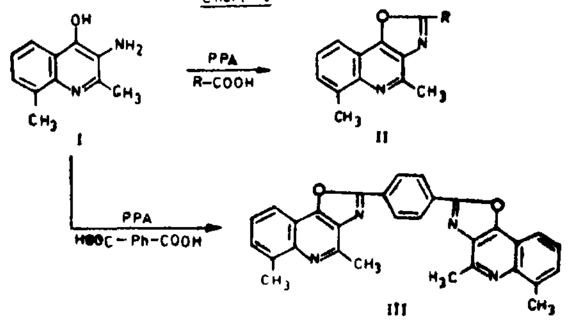


Chart II

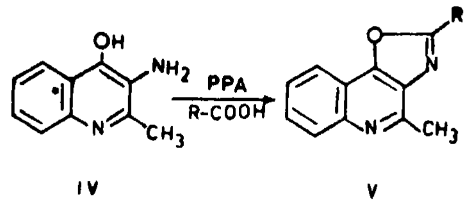
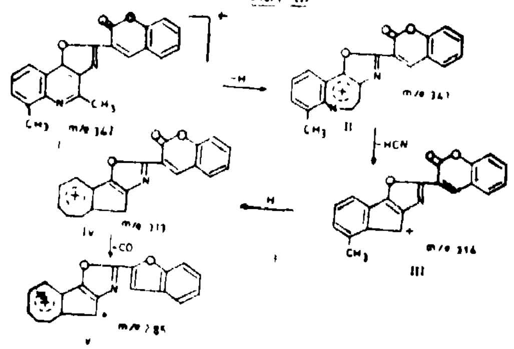


Chart - III



the mode of reduction. Fairly good yields are obtained in all cases and all the compounds possess intense fluorescence.

The above compounds have been characterised by U. V., I. R., mass and fluorescence spectral data.

U. V. Spectra :

The U. V. spectrum of the compounds have been recorded on Beckmann DK 2A spectrophotometer using dioxane as the solvent. The compounds exhibited two main regions of absorption around 340±20 nm and 280±10 nm, characteristic of coumarinyl substituted quinolino oxazoles.

The fluorescence spectra for all the compounds are measured on Beckmann DK 2A spectrophotometer

using dioxane as the solvent. The results are tabulated in *Table* 1.

TABLE 1

Sl. No.	2-(substituted) quinolino (3 : 4) oxazoles	max absorption nm	max emission nm	Difference	Colour observed
	9-Methyl quinolino (3 : 4) oxazoles				
1.	2-(p-Toluyl)	331	363.5	32.5	Violet
2.	2-(6′-Methyl-3′-coumarinyl)	361	458	97	Blue
3.	2-(8′-Methyl-3′-coumarinyl)	355	457	102	Blue
4.	2-(5′,6′-Benzo-3′-coumarinyl)	392	483	91	Green
5.	2-(6′-Bromo-3′-coumarinyl)	365	462	97	Blue
6.	2-(3′-Coumarinyl)	359	458	99	Blue
7.	*Bis*-1′,4′-(9-methyl-quinolino(3 : 4) oxazolo)benzene	352	406	54	Violet
	7,9-Dimethyl quinolino (3 : 4) oxazole				
8.	2-(Phenyl)	337	363	26	Violet
9.	2-(p-Toluyl)	337	362.5	25.5	Violet
10.	2-(Benzyl)	326.5	363	36.5	Light violet
11.	2-(2′-Naphthyl)	345	372	27	Intense violet
12.	2-(3′-Coumarinyl)	356	461	105	Blue
13.	2-(8′-Methyl-3′-coumarinyl)	362	459	97	Blue
14.	2-(6′-Methyl-3′-coumarinyl)	366	461	95	Blue
15.	2-(5′,6′-Benzo-3′-coumarinyl)	391	485	94	Green
16.	2-(6′-Bromo-3′-coumarinyl)	363	469	106	Intense blue
17.	*Bis*-1′,4′-(7,8-dimethyl quinolino (3 : 4) oxazolo) benzene	374	409	35	Violet

The information obtained from the fluorescence spectrum may be used in the evaluation of compounds as possible fluorescent brighteners for synthetic fibres, plastics etc. The fluorescent maxima of all these oxazoles have emission in the ideal range and therefore these compounds can be used as potential optical brighteners.

I. R. Spectra :

The I. R. spectra of these compounds have been recorded on Perkin-Elmer Model 137 in KBr. All the quinolino oxazoles exhibited a strong band around 1700±25 characteristic of coumarin carbonyl group. In addition to that, peaks at 1550 to 1580 cm^{-1}, 1100±50 cm^{-1}; 1350±10 cm^{-1} have also been found to be common, attributable to $>C=N$; $-C-O-C$ and $>C-N=$ of the oxazole system.

Mass Spectra :

Mass spectra were recorded on RMU-6L Mass spectrometer with inlet temperature ranging from 150° to 200° and an electron beam energy of 70 e.v. The major fragmentation pattern is the loss of $M^{+}-M\text{-}H^{\cdot}$ $-M\text{-}(H+HCN)$ as observed in the case of alkyl substituted quinolines[6]. It was followed by loss of carbon monoxide characteristic of coumarin moiety in the compounds. Molecular ion is the base peak.

Experimental

All the melting points are uncorrected.

Preparation of 3-amino-4-hydroxy-2-methyl quinoline :

2.7 gm of 3-benzene azo-4-hydroxy-2-methyl quinoline was mixed with 4 gm of sodium dithionite ; 30 ml ammonium hydroxide ; 30 ml water ; 15 ml rectified spirit and refluxed for half an hour. The hot solution was filtered and cooled. 3-Amino-4-hydroxy-2-methyl quinoline crystallised out, m.p. 255°.

Preparation of 2-(substituted)-9-methyl quinolino oxazole :

A mixture of 3-amino-4-hydroxy-2-methyl quinoline (0.005 mole) and appropriate acid (0.005 mole) was added to the poly phosphoric acid maintained at 100°. The reaction mixture was heated first at 150-60° for 2 hrs and then at 200-205° for a further period of 2 hrs. The reaction product was neutralised with conc. potassium hydroxide solution to get the corresponding 2-substituted-9-methyl quinolino (3 : 4) oxazoles. Recrystallisation was done with appropriate solvents as given in Table 2. 2-Substituted-7,9-dimethyl quinolino oxazoles were prepared by the same procedure starting with 2, 8-dimethyl-3-amino-4-hydroxy quinoline and respective carboxylic acids.

TABLE 2

Sl. No.	2-(substituted) quinolino (3 : 4) oxazoles	M.P. °C	% Yield	Solvent of recrystallisation
	9-Methyl quinolino (3 : 4) oxazoles			
1.	2-(3′-Coumarinyl)	250	60	Dioxane
2.	2-(Aryl)	177	65	Benzene
3.	2-(p-Toluyl)	170	65	Benzene
4.	2-(6′-Methyl-3′-coumarinyl)	250	60	Dioxane
5.	2-(8′-Methyl-3′-coumarinyl)	240	60	Dioxane
6.	2-(5′-6′-Benzo-3′-coumarinyl)	317	40	Dioxane
7.	2-(6′-Bromo-3′-coumarinyl)	278	60	Dioxane
8.	*Bis*-1′,4′-(9-methyl quinolino oxazolo) benzene	245	60	Dioxane
	7,9-Dimethyl quinolino (3 : 4) oxazoles			
9.	2-(Aryl)	178	65	Benzene
10.	2-(Benzyl)	273	65	Benzene
11.	2-(p-Toluyl)	186	65	Benzene
12.	2-(2′-Naphthyl)	212	65	Benzene
13.	2-(3′-Coumarinyl)	265	60	Dioxane
14.	2-(8′-Methyl-3′-coumarinyl)	310	60	Dioxane
15.	2-(6′-Bromo-3′-coumarinyl)	248	60	Dioxane
16.	2-(5′,6′-Benzo-3′-coumarinyl)	290	40	Dioxane
17.	2-(6′-Methyl-3′-coumarinyl)	257	60	Dioxane
18.	*Bis*-1′,4′-(7,9-dimethyl quinolino (3 : 4) oxazolo) benzene	225	60	Dioxane

Preparation of Bis 1', 4'-(7, 9-dimethyl quinolino oxazolo) benzene :

A mixture of 3-amino-4-hydroxy-2-methyl quinoline (0.01 mole) and terephthalic acid (0.005 mole) was added to the polyphosphoric acid maintained at 100°. The reaction mixture was heated first at 140° for 2 hrs and then at 160° for a further period of 4 hrs. The reaction product was neutralised with conc. potassium hydroxide solution, recrystallised from dioxane.

Acknowledgement

The authors are thankful to Prof. K. Koteswara Rao, Principal, Regional Engineering College, Warangal for providing necessary facilities. One of the authors (DAP) is thankful to C.S.I.R. organisation for sanctioning a Junior Research Fellowship; Sri P. S. Sastry, Assistant Professor, for the help in getting the spectra and to Sri G. V. P. Chandra Mouli, Teaching Assistant for the helpful suggestions.

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J. Indian Chem. Soc.,
Vol. LVII, August 1980, pp. 844-847

Complexation of Some Plant Auxins with Metal Ions of Biological Interest

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Manuscript received 12 October 1979, accepted 30 December 1979

In order to investigate chelation as a possible mode of action of plant auxins, the complexation of indole-3-acetic acid (IAA), indole-3-propanoic acid (IPA), indole-3-butanoic acid (IBA) and naphthalene-1-acetic acid (NAA) with Mg(II), Al(III), Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zr(IV), La(III) and Th(IV) have been investigated potentiometrically. Protonation constant of ligands and stepwise stability constant for metal-ligand complexes are reported at constant ionic strength (0.10M, KNO_3) and constant temperature (30°) in 50% aqueous dioxane (V/V). The general order of these stability constants with above auxins is found to be Th(IV)>Zr(IV)>Al(III)>Co(II)> Cu(II) Ni(II)>Fe(III). The stability constants of these metal-complexes are found to be almost same in the cases of IAA, IPA and IBA but are somewhat higher in the case of NAA. Since all auxins are biologically active and have approximately same value of stability constant, thus present investigation supports chelation as a possible mode of action of these auxins.

INDOLE-3-ACETIC acid, indole-3-propanoic acid, indole-3-butanoic acid and naphthalene-1-acetic acids are a few compounds which have auxin activity[1]. The first comprehensive studies in this field were made by Koepfli, Thimann and Went[2]. They concluded from their investigations using a range of compounds that an active growth substance must possess a ring system containing at least one double bond with a side chain carrying a carboxyl-group, there being at least one carbon atom between the ring and the –COOH group. In continuation of this hypothesis several theories[3-7] have been proposed but one that has been the most controversial was proposed by Heath and Clark[4] in which central idea was that auxin acts as a chelating agent. They worked with indole-3-acetic acid (IAA) and ethylenediaminetetraacetic acid (EDTA) but were unable to firmly establish their hypothesis. However, Cohen and his coworkers[7] were able to determine the stability constants of Cu(II) ion with indole-3-acetic acid and naphthalene-1-acetic acid (NAA) in 50% ethanol. This evidence up to some extent supports chelation as a possible mode of action for these auxins. These findings were also confirmed by Recaldin and Heath[8]. A mechanism, proposed by Van Overbeek[9] for auxin activity, retains the best feature of this hypothesis of two point attachment. A considerable research has been carried out to understand the origin, nature and physiological changes of these compounds. Some workers[10-12] do not agree that auxin activity is due to chelation. Jensen[13] also indicates that chelation is not the mode of action of plant auxins. Thus, in order to explore further chelation as a possible mode of action of these auxins a detailed equilibrium analysis of the complexation of indole-3-acetic acid (IAA), indole-3-propanoic acid (IPA), indole-3-butanoic acid (IBA) and naphthalene-1-acetic acid (NAA) with some metal ions of biological interest has been carried out potentiometrically employing Bjerrum-Calvin pH-titration technique[14-16] as employed by Irving and Rossotti[17].

Materials and Method : The ligands were obtained direct from Fluka AG, and were used after further purification. A 50% aq. dioxane (V/V) media was analysed to keep the ligands and most of their complexes *in* solution. Stock solutions of Mg(II), Al(III), Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zr(IV), La(III) and Th(IV) were prepared from analytical grade metal nitrates and standardized by titrating with disodium salt EDTA. Carbonate-free sodium hydroxide was prepared and standardized by titrating with potassium hydrogen phthalate (B.D.H. AnalaR, dried at 120° for two hours). Carbon dioxide free double distilled water was used for preparation of all the solutions. A Beckman pH-meter having glass electrode and calomel electrode assembly was used to record the pH-values.

The mixtures of (a) nitric acid and potassium nitrate, (b) mixture (a) and ligand solution and (c) mixture (b) and metal solution were prepared for each system (total volume 50 ml) and titrated against standard carbonate-free sodium hydroxide at constant ionic strength 0.10M(KNO_3) and temperature 30° in 50% aq. dioxane (V/V). The ratio of metal-ligand concentration was maintained 1 : 5 in order to satisfy the highest co-ordination number of the metal. Each of the titrations was repeated several times to get reproducible results. From the shifts in the pH-titration curves, values of the average number of protons associated with ligands ($\bar{n}_A$), the average number of ligands associated with

a metal ion ($\bar{n}$) and the free ligand exponent (pL) were calculated by Irving-Rossotti's[17] computational methods.

Results and Discussion

Proton-Ligand System : The proton-ligand formation curves (Fig. 1) and the titration curves having only one buffer region irrespective of the ligand employed clearly shows the equilibria $HL \rightleftharpoons H^{+} + L^{-}$. From the proton-ligand formation curves

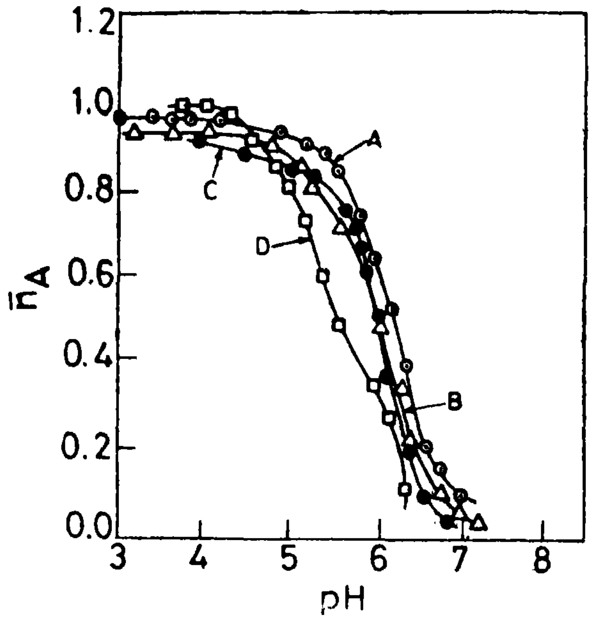


Fig. 1. Proton-Ligand Formation Curves :
A : IAA (—○—○—○—), B : IPA (—△—△—△—) ;
C : IBA (—●—●—●—) ; D : NAA (—□—□—□—).

the values of protonation constants (log K_1^H) were obtained directly by interpolation at half $\bar{n}_A$ values. These values are recorded in Table 1. An examination of these values shows that the protonation constants of IAA, IPA and IBA are almost same. A slight difference may be expected due to increase in chain length.

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS OF IAA, IPA, IBA and NAA
Temp. 30°C (μ = 0.1*M*)

Acid	Protonation Constant (log K_1^H)
Indole-3-acetic acid	6.26
Indole-3-propanoic acid	6.15
Indole-3-butanoic acid	6.15
Naphthalene-1-acetic acid	5.60

Metal-Ligand System : The metal titration curves were well separated from respective ligand titration curves. The metal ligand formation curves (Figs. 2-5) were obtained by plotting $\bar{n}$ against pL corresponding to each ligand. However, with more addition of alkali, at higher pH-values, precipitations occur and may be ascribed to hydrolytic effects. Hence $\bar{n}$ calculations were done before the point of precipitation.

Interaction of IAA, IPA and IBA with Metal Ions : All the metal ligand formation curves, except Th(IV)-IPA and Th(IV)-IBA formation curves (Figs. 3 & 4, curves F) are complete at both the ends. From complete formation curves (Figs. 2-4) the values of stepwise formation constants were evaluated by interpolating at half $\bar{n}$ values, 'Mid point' and 'correction term' method was also applied since K_1 & K_2 values are not very far apart and the curves are symmetrical at mid points. For incomplete formation curves the values of log K_2, log K_3 and log K_4 were computed by 'correction term' and 'successive approximation methods' and the values of log K_1 were obtained from equation log K_1K_2 = $2pL$. These values of formation curves for Fe(III) system could not be obtained due to hydrolytic effects at very low pH-values. No complexation could be demonstrated with Mg(II), Ca(II) and La(III) ions.

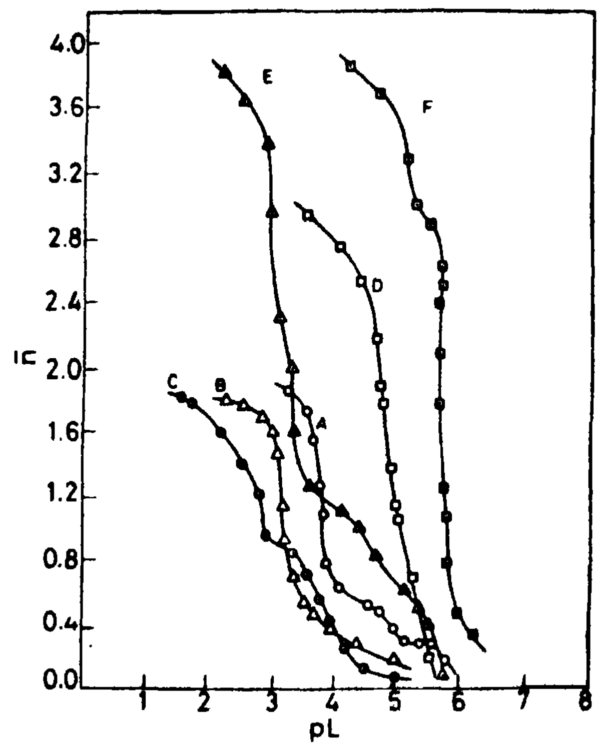


Fig. 2. Metal-Ligand Formation Curves :
A : Cu(II)-IAA ; B : Ni(II)-IAA ;
C : Co(II)-IAA ; D : Al(III)-IAA ;
E : Zr(IV)-IAA ; F : Th(IV)-IAA.

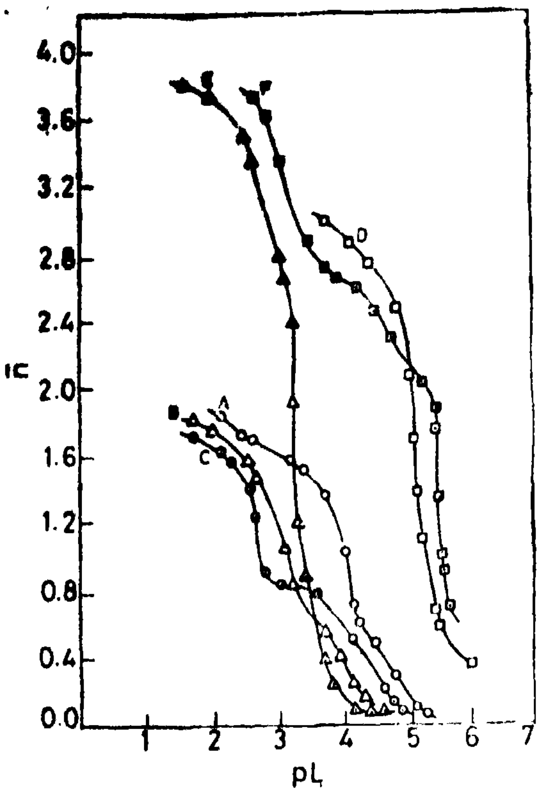


Fig. 3. Metal-Ligand Formation Curves :

A : Cu(II)-IPA ; B : Ni(II)-IPA ,
C : Co(II)-IPA ; D : Al(III)-IPA ,
E : Zr(IV)-IPA ; F : Th(IV)-IPA.

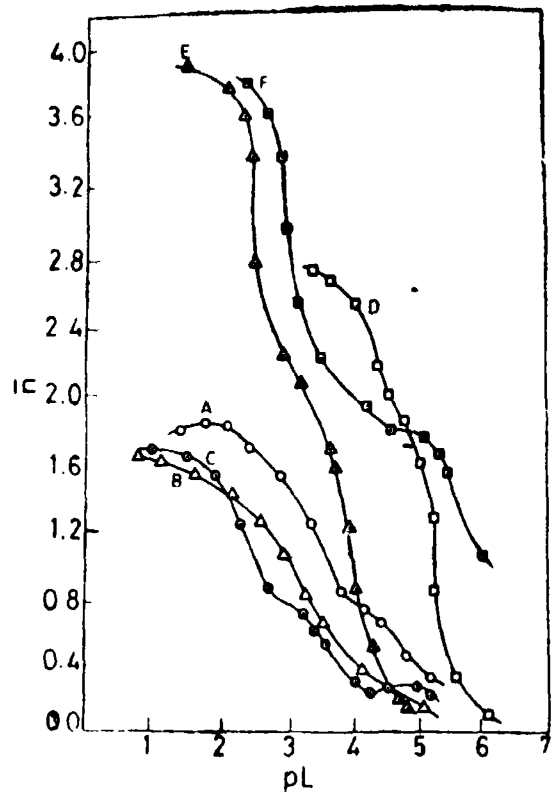


Fig. 4. Metal-Ligand Formation Curves :

A : Cu(II)-IBA , B : Ni(II)-IBA ;
C : Co(II)-IBA , D : Al(III)-IBA ,
E : Zr(IV)-IBA , F : Th(IV)-IBA.

Interaction of NAA with Metal Ions : An examination of the formation curves (Fig. 5) shows that the curves for Cu(II)-NAA, Co(II)-(NAA) and Ni(II)-(NAA) systems are complete but the formation curves for Al(II)-NAA, Zr(IV)-NAA and Th(IV)-NAA are incomplete in the lower half portion of the curves and due to their symmetrical nature the methods of interpolation at half n̄, 'correction term' and 'successive approximation' were applied as discussed above. For the evaluation of log K_1 values for incomplete formation curves the same equation log K_1 $K_2 = 2pL$ was used. With naphthalene-1-acetic acid also no interaction with Mg(II), Ca(II) and La(III) could be observed. The values of stability constants are reported in Table 2.

No significant differences in the overall stability constant values and hence in the chelating ability were found among the four auxins studied here. A slight variation may be expected due to the increase of methylene groups in the chain having carboxyl group. In these auxins the ring of considerable aromatic character seems essential for auxin activity. The general order of stability of complexes of metal

TABLE 2—METAL-LIGAND STABILITY CONSTANTS OF VARIOUS METALS OF BIOLOGICAL INTEREST WITH IAA, IPA, IBA and NAA (T = 30°C, μ = 0.1*M*)

Metal Complex	log k_1	log k_2	log k_3	log k_4	log β
IAA-Complex					
Al(III)	5.30	4.80	4.40	—	14.55
Co(II)	3.95	2.40	—	—	6.35
Ni(II)	3.60	3.05	—	—	6.65
Cu(II)	4.70	3.70	—	—	8.40
Zr(IV)	5.65	3.40	3.00	2.80	14.85
Th(IV)	5.80	5.65	5.60	5.00	22.05
IPA-Complex					
Al(III)	5.70	5.20	4.80	—	15.70
Co(II)	4.25	2.50	—	—	6.75
Ni(II)	3.80	2.70	—	—	6.50
Cu(II)	4.50	3.50	—	—	8.00
Zr(IV)	3.70	3.30	3.25	2.55	12.80
Th(IV)	5.65	5.55	4.50	3.00	18.70
IBA-Complex					
Al(III)	5.45	5.20	4.15	—	14.80
Co(II)	3.70	2.00	—	—	5.70
Ni(II)	3.85	1.80	—	—	5.65
Cu(II)	4.75	2.80	—	—	7.55
Zr(IV)	4.40	3.85	2.70	2.60	13.55
Th(IV)	6.65	5.55	3.30	2.95	18.45

(Table 2 Contd.)

NAA-Complex					
Al(III)	7.15	5.45	4.90	—	17.50
Co(II)	3.70	3.50	—	—	7.20
Ni(II)	3.75	2.50	—	—	6.25
Cu(II)	3.60	3.40	—	—	7.00
Zr(IV)	5.80	5.00	4.35	3.60	18.75
Th(IV)	8.00	7.30	6.15	5.15	26.60

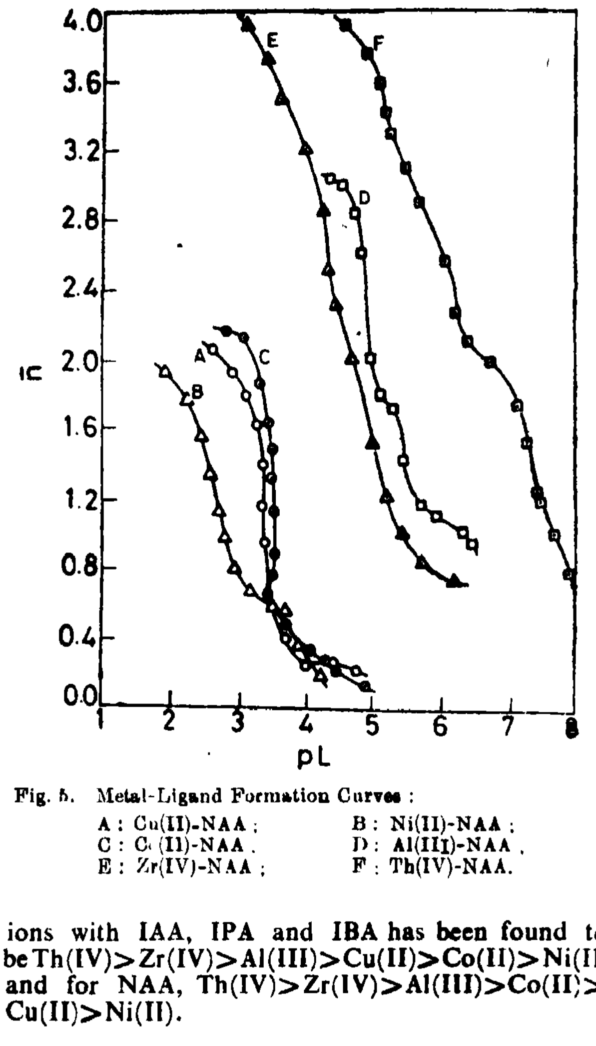


Fig. 5. Metal-Ligand Formation Curves :
A : Cu(II)-NAA ; B : Ni(II)-NAA ;
C : Co(II)-NAA . D : Al(III)-NAA ,
E : Zr(IV)-NAA ; F : Th(IV)-NAA.

ions with IAA, IPA and IBA has been found to be Th(IV)>Zr(IV)>Al(III)>Cu(II)>Co(II)>Ni(II) and for NAA, Th(IV)>Zr(IV)>Al(III)>Co(II)> Cu(II)>Ni(II).

An examination of stability constant values of these auxins indicates that the rate of metal dependent reactions will have to be illucidated before the mode of auxins action is understood. The stability constant of various metals are found to be almost same in case of IAA, IPA and IBA but is somewhat higher with NAA. Since all auxins are biologically active and have approximately same values of stability constants, thus present investigation supports chelation as a probable mode of action of these auxins.

Acknowledgement

The financial support of this work from ICAR, New Delhi is gratefully acknowledged. The authors are grateful to Dr. J. B. Singh (G. S. V. M. Medical College, Kanpur) for providing some experimental facilities.

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NOTES

Oxovanadium and Oxouranium Complexes of 3-7 Dimethyl 7-Hydroxy Octane-1-al

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Manuscript received 20 February 1979, revised 11 February 1980, accepted 19 May 1980

3-7 dimethyl 7-hydroxy octane 1-al forms 1 : 2 complexes with VO_2(II) and UO_2(II) and their structures have been characterised on the basis of elemental analysis, conductometric, *p*H metric, spectrophotometric and infrared studies. Stability constants of these complexes as calculated by Bjerrum method were found to be 1.08×10^{-2} and 1.00×10^{-2} for VO_2(II) and UO_2(II) complexes respectively.

Metal complexes of 3-7 dimethyl 7-hydroxy octane 1-al were studied for the first time by the authors. 3-7 dimethyl 7-hydroxy octane 1-al is an aldehydic monoterpenic alcohol[1]. Having an aldehydic group and a hydroxyl group, it shows great tendency towards complex formation. The present communication deals with the preparation and characterisation of metal complexes of vanadyl and uranyl ions with 3-7 dimethyl 7-hydroxy octane 1-al and their stabilities were calculated by Job's and Bjerrum methods.

Experimental

3-7 dimethyl 7-hydroxy octane 1-al, which was procured from M/S. H. Kelkar Co., Kerala was purified by column chromatography and its purity was further checked on T.L.C. plates.

All chemicals used were of AnalaR (B.D.H) grade. A 0.1*M* standard stock solution of vanadyl sulphate was prepared in doubly distilled water and a 0.1*M* stock solution of uranyl nitrate was prepared in ethanol. Standard stock 0.01*M* solution for 3-7 dimethyl 7-hydroxy octane 1-al (ligand for our purpose) was prepared in ethanol.

All conductometric studies were carried out on Toshniwal conductivity bridge model CLO1/02A with a dip type cell. An Elico *p*H meter model LI-10 was used for *p*H metric titrations. Hydrogen and glass electrodes were used for *p*H metric determination. Spectrophotometric studies were carried out on Bausch and Lomb spectronic-20 type of spectrophotometer. Infrared spectra of the complexes were recorded in KBr disc on a Perkin-Elmer model 221 in the region 4000 cm^{-1} to 600 cm^{-1}.

The complexes were isolated in aqueous ethanolic and ethanolic media. Ethanolic solution of ligand and aqueous solution of vanadyl sulphate were mixed in 2 : 1 ratio. Similarly ethanolic solution of ligand and uranyl nitrate were mixed in 2 : 1 stoichiometric ratio. The solutions were refluxed on water bath for 48 hours, on cooling greenish powdery mass was separated out for vanadyl complex and greenish yellow crystals of uranyl complex were separated out. The complexes were washed several times with the solvent and vacuum dried. The complexes were microanalysed for carbon and hydrogen and observed values were in good agreement with the calculated one. These values are given below :

	%of carbon		%of hydrogen		%of metal	
	Found	Calc.	Found	Calc.	Found	Calc.
Vanadyl complex	23.3	23.2	3.9	3.6	11.05	11.36
Uranyl complex	32.4	32.1	5.6	5.3	35.31	35.35

Results and Discussion

Reverse conductometric titrations[2] at 0.01*M* to 0.1*M* concentrations for metal and ligand were performed at room temperature. *p*H metric titrations were performed by Bjerrum method as modified by Irving and Rossotti[3]. The complexes were stable at *p*H 6.5 to 8.2. Spectrophotometric studies were carried out by Job's method[4] of continuous variation at 540 nm and 490 nm for green and yellowish green complexes of vanadyl and uranyl ions. The complexes obey Beer's law under the concentration range 0.005*M* to 0.01*M*.

The spectrophotometric studies of the complexes were performed at 540 nm and 490 nm for vanadyl and uranyl complexes respectively. Transitions are different for both the complexes which are helpful for identification and quantitative analysis of the metal ions. Wave number and frequency of the monochromatic light were found to be in the range of 20.408 cm^{-1} and 6.122 cm^{-1}. The molar extinction coefficients (Σ) of the complexes were found 300 lit/mole, cm and 350 lit/mole, cm for vanadyl and uranyl complexes respectively.

Information regarding the nature of bonding was obtained by subjecting the ligand and complexes for IR studies. According to the structure of hydroxy citronellal, two positions may be prone to coordinate with metal ions, they are aldehyde group and hydroxy group. In both of these complexes the bands at 3600 cm^{-1} (due to hydroxyl group) and at 1650 cm^{-1} (due to aldehyde group) disappears.

The hydroxycitronellal therefore must be acting as bidentate ligand.

The metal ligand stability constants were calculated by Job's method[5] of formula

$$K=\frac{X}{(a_1-X)(b_1-X)}=\frac{X}{(a_2-X)(b_2-X)}$$

where a_1, a_2 are the concentrations of metal and b_1, b_2 are the concentrations of ligand at different dilutions.

Values of stability constants were further confirmed by Bjerrum method[6] as modified by Irving and Rossotti

$$\bar{n}=\frac{(v''-v')\ N+E^{\circ}+TL^{\circ}\ (Y-\bar{n}A)}{(v^{\circ}+v')\ \bar{n}ATM^{\circ}}$$

All the above studies confirmed the complexation ratio to be 1 : 2.

Acknowledgement

The author's thanks are due to C.S.I.R. for the award of a S.R.F. to one of us (M.N.)

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Determination of Stability Constants of 5-Methyl-Salicylidene-*p*-Methylaniline Complexes with Y^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+} and Dy^{3+}

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Manuscript received 21 April 1979, revised 17 April 1980, accepted 12 June 1980

IN the present communication the successive stability constants of the complexes of 5-methyl-salicylidene-*p*-methylaniline with various trivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum *p*H titration technique as adopted by Irving and Rossotti[1].

Experimental

The ligand 5-methyl-salicylidene-*p*-methylaniline was prepared by the method described in literature[2], and was repeatedly crystallised. (Observed m.p. 106°, Reported m.p. 106°).

Dioxan used was purified by usual method reported in literature[3]. The medium of titration was 75 : 25 percent (v/v) dioxan-water mixture. Sodium perchlorate was added to maintain a constant ionic strength. The titrations were carried out in nitrogen atmosphere.

The metal perchlorates were prepared from the metal carbonates of A.R. grade supplied by S.D. Lab. Chem., Bombay, using perchloric acid of A.R. grade. All these were standardised complexometrically[4] by E.D.T.A. titrations. All the measurements were carried out at 25 ±0.1°. The Corning Model 12 with a combined glass electrode and a calomel electrode was used.

The experimental details and computational methods are the same as described in the earlier communication[5]. The experimental method of Irving and Rossotti[1] was applied to find out the values of $\bar{n}$ and *p*L. The appropriate corrections for the H^+ ion concentrations have been made as per the work of Irving and Mahnot[6] and the values have been accordingly modified. Appropriate ion corrections were made at high *p*H. The titrations were performed in duplicate to test the reproducibility.

Results and Discussion

It may be stated here that the reagent does not undergo hydrolysis under the experimental conditions described. This was indicated by rapid attainment of equilibrium during the titration and by the absence of any significant drift in *p*H meter readings even after one hour.

In the ligand it is the phenolic (OH) group which takes part in the complex formation and the proton is replaced from it by metal ions during chelation. Since only one proton per ligand molecule is liberated during complexation, 'Y', the number of dissociable protons attached to each ligand molecule is one.

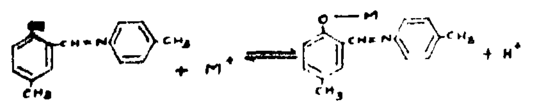
The curve between 'B' and the corresponding $\bar{n}_A$ value was plotted to get the formation curve. The formation curve extends over a range of $0.35<\bar{n}_A<1.95$ and is wave-like. The value of pK_1^H, which corresponds to the association of phenolic (OH) group, was evaluated from the half integral point at $\bar{n}_A=0.5$, while that of pK_2^H, which corresponds to the association of proton to imino-nitrogen was

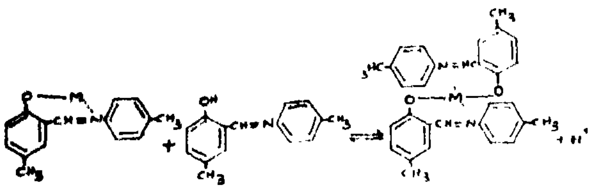
obtained at $\bar{n}_A = 1.5$. These values were further corroborated from the plots of

$$\log\left[\frac{\bar{n}_A}{1-\bar{n}_A}\right] \text{ vs B and } \log\left[\frac{2-\bar{n}_A}{\bar{n}_A-1}\right] \text{ vs B respectively.}$$

$\bar{n}$ and pL values were calculated and $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of the metal complex-ion equilibria. From the formation curves, the values of stability constants log K_1 and log K_2 were evaluated which correspond to 1 : 1 complex at $\bar{n} = 0.5$ and 1 : 2 complex at $\bar{n} = 1.5$ respectively. These were further corroborated by plotting log $\left[\frac{\bar{n}}{1-\bar{n}}\right]$ vs pL and log $\left|\frac{2-\bar{n}}{\bar{n}-1}\right|$ vs pL graphs, respectively.

The formation of 1 : 1 and 1 : 2 complex is represented below :





In all the cases, stabilities of 1:1 complexes were evaluated, while in the cases of Y^{3+}, Nd^{3+} and Gd^{3+} stabilities of 1 : 2 complexes were also evaluated. The log K_2 for others could not be evaluated due to precipitation probably due to metal ion hydrolysis. The order of stability of trivalent metal-chelates was found to be

$$Y^{3+} > Pr^{3+} > Gd^{3+} > Dy^{3+} > Nd^{3+}$$

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES*

t = 25°C μ = 0.1 *M*

Cations	H^+	Y^{3+}	Pr^{3+}	Nd^{3+}	Gd^{3+}	Dy^{3+}
Log K_1	11.38	7.82	7.73	6.88	7.66	7.46
Log K_2	3 80	7.02	—	6.18	6.83	—

* For proton association (H^+), K_1 and K_2 correspond to the species LH and LH_2^+ respectively, while for metal ions K_1 and K_2 correspond to the species ML_1 and ML_2 respectively.

Acknowledgement

The authors wish to record their sincere thanks to Dr. D. G. Vartak, B.A.R.C., Bombay for the valuable suggestions and to Prof. A. P. Rao, Vice-Principal, Ramnarain Ruia College, Bombay, for his kind and continuous encouragement in accomplishing this work.

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Quinoxaline Complexes with Some Mercury(II) Salts

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Manuscript received 25 June 1979, revised 5 May 1980, accepted 21 May 1980

THE complexes of quinoxaline (Q) with several transition metal salts have been studied by various workers[1-5] and here are described those formed by interaction with Hg(II) chloride, bromide, cyanide and thiocyanate. These complexes have been characterized by molar conductance, molecular weight, IR and far-IR spectral measurements down to 200 cm^{-1}.

The chloro-, bromo- and cyano-complexes were prepared by adding an excess of the ligand solution in ethanol to a hot solution of the metal salt in the same solvent. The thiocyanato complex was prepared by boiling a suspension of the metal thiocyanate with an excess of the ligand in ethanol and filtering the solution hot. The complexes which precipitated or crystallized out were filtered, washed with ethanol and dried in vacuo. $Hg(Q)Cl_2$: m.p. 256 [Found : Hg, 50.40 ; Cl, 17.29, Calc. : Hg, 49.87 ; Cl, 17.70%] : $Hg_2(Q)Br_4$: m.p. 243 [Found : Hg, 46.58 ; Br, 36.67, Calc. : Hg, 47.07 ; Br, 37.64%] : $Hg(Q)(CN)_2$: m.p.>290° [Found : Hg, 52.50 : Calc. : Hg, 52.35%] : $Hg(Q)(SCN)_2$: m.p. 176 d. [Found : Hg, 44.12 ; SCN, 26.32, Calc. : Hg, 44.84 ; SCN, 26.00%].

Molar conductance of $10^{-3}M$ solutions in DMF (Philips Conductivity Bridge) indicate them to be non-electrolytes, except the thiocyanato-complex which acts as a weak electrolyte. The IR spectra of

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the complexes recorded in Nujol mulls with a Perkin-Elmer 621 spectrophotometer are similar to those of quinoxaline complexes with other metal salts[1-5], conforming coordination of the two ligand-N atoms to different metal ions, the ligand thus acting as a bidentate bridge (steric positions of nitrogen atoms in quinoxaline precludes chelation). In addition to the absorption bands due to coordinated quinoxaline, the far-IR spectra of the chloro- and bromo-complexes show the halogen dependent terminal[6,7] Hg – X stretching modes at 320 and 225 cm^{-1}, respectively. The bridging Hg – Br stretching mode in bromo-complex expected at ~150 cm^{-1} could not be recorded with the present range of the spectrophotometer. However, the molecular weight of the bromo-complex determined by Rast's method (obs. 810, calc. 850) is consistent with the dimeric structure. The molecular weights of the other complexes could not be determined by this method as they were insoluble in camphor.

The IR spectrum of the cyano-complex shows additional absorption bands at 2183, 421 and 325 cm^{-1} which are identified as ν(CN), ν(HgC) and δ(HgCN) modes respectively, due to coordinated terminal cyano groups[8]. The frequency of ν(CN) suffers a significant negative shift when the cyano bridges break down and mercury(II) cyanide complexes with terminal cyano groups absorb at lower frequencies than pure mercury(II) cyanide containing bridging cyano groups[8]. Furthermore, ν(HgC) shift to higher frequencies in complexes containing bridging cyano groups and this positive shift may be attributed to coupling of ν(HgC) with ν(CN) in the HgCN part of the molecule. Since terminal cyano groups absorb at lower frequencies than pure $Hg(CN)_2$, the terminal ν(HgC) and δ(HgCN) modes would also be expected to absorb at lower energies as are observed here for terminally bonded cyano groups[8]. The thiocyanato-complex shows absorption bands at 2117, 717 and 439 cm^{-1} which are assigned as ν(CN), ν(CS) and δ(SCN), respectively, of the coordinated thiocyanato groups. The frequencies of these modes are consistent with those normally associated with terminal S-bonded thiocyanato groups[9,10].

From spectral results it is suggested that chloro-, cyano-and thiocyanato-complexes have polymeric four-coordinated tetrahedral geometry around the metal atoms with two terminally bonded anionic groups and the two nitrogens of the bidentate bridging quinoxaline molecules. The bromo-complex has been assigned a dimeric four-coordinated structure involving both bridging as well as terminal bromide ions.

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Optimal Temperature (T_{opt}) for Maximal Thermal Conductivity (K_{max}) of Solids at Low Temperatures**

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Manuscript received 28 April 1980, accepted 12 June 1980

IN continuation of our earlier communication[1], we now discuss the success of the said equation by calculating the T_{opt} value for many solids to the second order of approximation (S.O.A.) and examine the improvement achieved thereby over the value obtained for the same to the first order of approximation (F.O.A.) in respect of the latest reported[2,3,4] observed values.

The three-term-thermal conductivity equation, which has been successfully utilized for obtaining a meaningful and informative reduced low-temperature thermal conductivity expression[5] for solids of widely varying nature, embracing metals, semiconductors, insulators including molecular crystals and chemical compounds, has been expressed[1] as

$$K = \frac{T}{\alpha + \delta T^2 + \gamma T^3} \quad \text{or} \quad \frac{1}{K} = \frac{\alpha}{T} + \delta T + \gamma T^2 \qquad \ldots (1)$$

from which the expression for T_{opt} is obtained[1] as

$$T_{opt} = (\alpha/4\gamma)^{1/3}[\{1 + \sqrt{1 - \delta^3/27\alpha\gamma^2} - \delta^3/54\alpha\gamma^2\}^{1/3} + \{1 - \sqrt{1 - \delta^3/27\alpha\gamma^2} - \delta^3/54\alpha\gamma^2\}^{1/3}] - \delta/6\gamma \qquad \ldots (2)$$

where, according to the most recent views[6], α, δ and γ are constants being respectively related to the scattering of phonons by geometrical factors including impurities, the effect of anharmonic coupling

** The paper has been submitted for Oral presentation at the Convention of Chemists to be held at I.I.T., Bombay (Powai) in December, 1980.

TABLE 1

Solids	Calculated values for $T_{opt(F.O.A.)}$ (recorded up to the second place of decimal)	Difference between the T_{opt} values for the two approximations (recorded up to the third place of decimal)	Calcd. values for $T_{opt(S.O.A.)}$ (recorded up to the second place of decimal)	Observed value[2,3,4] for T_{opt}	%deviation of $T_{opt(F.O.A.)}$ value from the observed value[2,3,4] (recorded up to the first place of decimal)	%deviation of $T_{opt(S.O.A.)}$ value from the observed value[2,3,4] (recorded up to the first place of decimal)
1	2	3	4	5	6	7
Silicon	22.14	2.100	24.24	25	11.44	3.0
Tin	1.97	0.045	2.01	2	1.5	0.5
Iron	14.20	0.061	14.26	15	5.3	4.9
Niobium	11.44	0.400	11.84	13	12.0	8.9
Palladium	8.54	0.018	8.56	9	5.1	4.8
Platinum	7.96	0.030	7.99	8	0.5	0.1
Osmium	15.63	0.050	15.68	20	21.9	21.6
Rhodium	16.41	0.413	16.82	18	8.8	6.5
Ruthenium	19.65	0.200	19.85	20	1.7	0.8
Thorium	7.56	0.044	7.60	8	5.5	5.0
Tungsten	8.76	0.145	8.91	10	12.4	10.9
Zinc	4.70	0.020	4.72	6	21.6	21.3
Neon	3.14	0.074	3.21	3.5	10.2	8.3
Quartz	7.75	0.027	7.78	9	14	13.5
Synthetic Sapphire	54.25	5.582	59.83	56	3.1	6.8

of phonons[7] and phonon-phonon interaction. T_{opt} to the first order and second order of approximations are obtained as

$$T_{opt(F.O.A.)} = (\alpha/2\gamma)^{1/3} - \delta/6\gamma \quad \dots (3)$$

and

$$T_{opt(S.O.A.)} = (\alpha/2\gamma)^{1/3}\{1+(2^{2/3}.\delta^2)/(36\alpha^{8/3}.\gamma^{4/3})\} - \delta/6\gamma \quad (4)$$

from which we obtain

$$T_{opt(S.O.A.)} - T_{opt(F.O.A.)} = (\alpha/2\gamma)^{1/3}\{(2^{2/3}.\delta^2)/(36\alpha^{8/3}.\gamma^{4/3})\} \quad \dots (5)$$

$T_{opt(S.O.A.)}$ value for fifteen solids of various nature has been calculated by utilizing equation (5), in combination with our results for $T_{opt(F.O.A.)}$ reported earlier[1]. The values are recorded in Table 1 which also enlists the values for $T_{opt(F.O.A.)}$ and the differences between the said two approximations. The percentage disagreement from the observed[2,3,4] values of the two approximations has also been recorded in the table for easy and ready reference.

Considering the reported[2,3,4] uncertainties in the observed values of the solids, discussed in this paper, the results obtained appear to contribute fairly towards the success of the three-term-empirical equation published elsewhere[1]. As expected, the $T_{opt(S.O.A.)}$ value, in general, shows an improvement over the $T_{opt(F.O.A.)}$ value, being closer to the observed value, in all cases. The synthetic sapphire is, however, an exception. This may, perhaps, be due to the probability of greater inaccuracy in the determination of its thermal conductivity in the low-temperature region.

Acknowledgement

One of us (SNJ) is thankful to the UGC for the award of Teacher Fellowship under the Faculty Improvement Programme.

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The Kinetics of Oxidation of D (+) Glucose by Potassium bromate in Acid Medium

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Manuscript received 18 August 1978, revised 19 February 1980, accepted 21 May 1980

THE kinetics of the oxidation of D(+)glucose has been extensively studied using different oxidising agents, e.g., Ce(IV)[1], Cu(II)[2] in alkaline medium, ammoniated $AgNO_3$[3], $Pb(OAc)_4$[4], $K_3Fe(CN)_6$ in

aqueous NaOH[5], potassium hexacyanoferrate[6], $K_2S_2O_8$[7], aqueous chlorine[8], vanadium[9], H_2O_2[10], HNO_3[11] and $KMnO_4$[12]. In continuation of our recent interest[13] in oxidation of organic substrates, we now report the kinetic study of oxidation of D(+)glucose by $KBrO_3$ in acid medium.

Experimental

The stock solutions of dried, at 120° for 2 hrs, $KBrO_3$ (Baker analysed grade) were prepared in conductivity water. D(+)glucose, H_2SO_4 and K_2SO_4 used were of BDH, AR quality and all other chemicals used were of highest quality. The reactions were studied in a thermostat (±1°). The rate of reaction was followed by estimating residual $KBrO_3$ by standard iodometric method[14,15]. The ionic strength was maintained throughout at 0.52 by adding K_2SO_4, if necessary.

The order with respect to $KBrO_3$ was determined by isolation method whereas in case of D(+)glucose and H^+ it was determined by Vant Hoff's differential method.

Observations :

TABLE 1

Temperature 50°C

Concentration of reactants	Mean value of $K \times 10^3 min^{-1}$	Order
D(+)glucose = 0.1000*M*		
$KBrO_3$ = 0.0007*M*		
H_2SO_4		
0.08783*M*	0.4102	2.05 } = 2
0.1094*M*	0.6688	2.04 }
0.1318*M*	0.8487	
$KBrO_3$ = 0.0007*M*		
H_2SO_4 = 0.1706*M*		
D(+)glucose		
0.025*M*	0.3146	—
0.050*M*	0.8130	1.2 } = 1
0.1000*M*	1.5660	1.06 }
H_2SO_4 = 0.1706*M*		
D(+)glucose = 0.1000*M*		
$KBrO_3$		
0.0007*M*	1.566	1 }
0.0005*M*	1.052	1 } = 1
0.0002*M*	1.498	1 }

TABLE 2

Concentration of D(+)glucose = 0.1000*M*; ,, ,, $KBrO_3$ = 0.0007*M*; ,, ,, H_2SO_4 = 0.1706*M*

Temperature 50°C (Except for K^a)

K^{a*}	K^b	K^c	K^d	K^c
4.958	2.79	5.590	1.540	1.530
6.960	4.50	9.760	1.600	1.430
7.730	5.92	10.730	1.520	1.185
20.470	9.60	30.970	1.590	1.034

Effect of temperature K^a = 35°C, 40°C, 45°C and 55°C,
Effect of solvent polarity = (%H_2O-%CH_3COOH) K^b = 95-5, 90-10, 85-15 and 80-20
Effect of high acidity K^c H_2SO_4 = 0.3282*M*, 0.4593*M*, 0.6562*M* and 0.9711*M*
Effect of ionic strength $K^d(KNO_3)\sqrt{\mu}$ = 0.75, 0.80, 0.85 and 0.90
$K^e(K_2SO_4)\sqrt{\mu}$ = ,, ,, ,, ,,
* values of rate constant are in 10^3 min^{-1}.

Results and Discussion

The study of the kinetics of oxidation of D(+) glucose has been carried out, in presence of H^+ ions, at a constant ionic strength of 0.52, by $KBrO_3$. The order with respect to D(+)glucose, H^+ and $KBrO_3$ has been found to be one, two and one respectively (cf Table 1). But for a given particular concentration of H^+ the total order of reaction gets reduced to two. The change in ionic strength, produced by KNO_3 (1-1) does not affect the rate constant. But in case of K_2SO_4 (1-2) the rate decreases as Bronsted's equation is not rigidly applicable in this case[16]. This independence of rate on ionic strength leads to the suggestion that at least one of the reacting species is a neutral molecule. The effect of solvent polarity (different AcOH-water mixture) shows regular increment in the rate with the increase of acetic acid to water proportion. The plot of log K and AcOH-water composition (i.e. 1/D) is linear having positive slope, thus broadly classifying bromate oxidation of D(+)glucose as as a positive ion-dipole type of reaction[17]. The effect of acidity dependence reveals that plot of logH^+ and log K is linear thereby suggesting involvement of a solvent molecule in the transition state[18]. The plot of $\frac{1}{K}$ vs $\frac{1}{D+(glucose)}$ has been found to be linear with a positive intercept on Y axis and thus give evidence of a complex formation between D(+)glucose and a diprotonated bromate $(H_2Br^+O_3)$[19]. The change in temperature on reaction rate yielded values of energy of activation, temperature coefficient, frequency factor, entropy of activation and free energy of activation as 15.74 K cal, 2.05, 1.65×10^9 (sec^{-1}), −17.6 E. U. and 24.42 K cal respectively.

Thus based on above experimental findings the proposed reaction mechanism involves formation of $[H_2Br^+O_3]$ by the action of H_2SO_4 on $KBrO_3$. The diprotonated bromate ion reacts with glucose molecule to give a complex $[C_6H_{11}O_6^-BrO_3H]^+$. This complex breaks finally to give lactone of gluconic acid in presence of a nucleophilic reagent B.

The above mentioned lactone was characterised by TLC using solvent system isopropanol-pyridine-water-acetic acid [8 : 8 : 4 : 1] as product of the reaction. The other product Br^- ions was tested by $AgNO_3$ giving characteristic pale yellow precipitate soluble in liquor ammonia.

The stoichiometry of oxidation reaction could not be established due to the fact that Br_2 was liberated at higher $KBrO_3$ concentration which is needed for its determination. Moreover Br_2 was liberated usually within three hours of start of reaction under normal $KBrO_3$ concentration at 50°. The Br^- formed by the reduction of BrO_3^- to give

Br_2 is according to the reaction

$$BrO_3^- + 6H^+ + 5Br^- \rightarrow 3Br_2 + 3H_2O$$

This evolution of Br_2 created complexity, which is also an oxidising agent, in the determination of the stoichiometry of the reaction.

The rate law for the reaction is represented as

$$\frac{-d}{dt} Br(V) = K_4[Br(V)]\ [Glucose]\ [H^+]^2$$

Now for a definite H^+ concentration, which are reproduced in the system hence act as catalyst, the rate law reduces to

$$\frac{-d}{dt} Br(V) = K_5[Br(V)]\ [Glucose]$$

Acknowledgement

The authors are indebted to Prof. S. S. Tewari for providing all necessary help and to University Grants Commission for research fellowship to junior author (CDB).

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Effect of Halide Ions on Cathodic Polarization of Nickel in Presence of Dicyandiamide and Related Compounds in Sulphuric Acid

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Manuscript received 2 January 1979, revised 12 January 1980, accepted 4 March 1980

THE synergistic effect of anions and amines in corrosion inhibition of iron in acid solution has been investigated by a number of workers[1-4]. Also the adsorption of anions on metal surfaces has been investigated by different investigators[5-9]. However, such investigations on the effects of halides on the corrosion of nickel in acid solution are recent and rare[10-12]. The present investigation is concerned with the effect of halides on cathodic polarization of nickel in deaerated $1N$ sulphuric acid in presence of dicyandiamide, biguanide and guanyl urea.

Experimental

Nickel (99.9% purity) used as electrode, was in the form of beads of circular surface area 0.2 sq. cm. The galvanostatic method used for steady state polarization studies consisted of a constant current generator and one vernier potentiometer having different channels for measuring corrosion current and corrosion potential. All experiments were carried out at $25 \pm 1°$ in inert atmosphere. A saturated calomel electrode was used as reference electrode.

Results and Discussion

The results of the polarization measurements are generally interpreted in terms of Tafel parameters. The E_{corr}, cathodic Tafel slopes, exchange current densities (obtained by extrapolation method) have been tabulated in Table 1. It can be seen that the open circuit corrosion potential is gradually shifted from 232 mv (vs SCE) in pure sulphuric acid to 246 mv, 370 mv and 416 mv with the addition of chloride, bromide and iodide ions respectively. The open circuit corrosion potentials of nickel in sulphuric acid is 232 mv (vs SCE) and the addition of dicyandiamide, guanyl urea and biguanide shifts it to 216 mv, 217 mv and 242 mv. The corresponding changes of Tafel slopes are, however, not so marked in presence of organic compounds. The effect of halides on the exchange current densities is also quite apparent from the Table 1.

In presence of chloride ions, dicyandiamide and guanyl urea shift the open circuit potential to more negative direction but this shift is not so prominent in case of biguanide. Dicyandiamide and guanyl urea shift open circuit potential towards positive direction as compared to the solutions containing

TABLE 1—EFFECT OF HALIDE IONS ON THE CATHODIC POLARIZATION OF NICKEL IN 1N SULPHURIC ACID

Composition of solutions :

$10^{-3}M$ Inhibitor + $10^{-4}MK^{+}X^{-}$ + $1NH_2SO_4$ (X^{-}, halide)

Solution		Open circuit corrosion potential −mv ± 5mv	Equlb. exchange current density mA/cm²	Cathodic Tafel slope b_c mv/dec. ± 4mv
1N H_2SO_4		232	.0018	115
+ Cl^-		246	.0032	125
+	+ Dyc	280	.0042	130
+	+ Big	244	.0018	115
+	+ GU	362	.020	100
+ Br^-		370	.012	120
+	+ Dyc	415	.020	90
+	+ Big	423	.028	110
+	+ GU	260	.0022	120
+ I^-		416	.010	65/175
+	+ Dyc	330	.012	95
+	+ Big	265	.0025	115
+	+ GU	267	.004	125
	+ Dyc	216	.00075	115
	+ Big	242	.00034	110
	+ GU	217	.00024	105

Dyc : Dicyandiamide, Big : Biguanide, GU : Guanyl Urea.

only chloride or only inhibitor solution. In presence of bromide ions all these compounds shift the potential towards negative directions. It is interesting to note that the open circuit corrosion potentials of all the solutions containing iodide ions are more negative than those of the respective inhibitor solutions but more positive than that of iodide solution.

The Tafel slope and exchange current density for nickel are found to be 115 mv/decade and .0018 mA/cm² respectively. These parameters are in resonable agreement with those obtained by others for nickel taken in single crystal form and in different acid media[10,13,14]. The corrrosion potential of nickel in the ϕ-scale is +0.06 volts[3]. Thus it is quite resonable to assume that at this open circuit corrosion potential the surface charge on nickel is positive and would favour the adsorption of negatively charged ions. And thus, iodide ions, due to their large size and easily deformable electron shell, are most strongly adsorbed. However, the existence of two Tafel slopes in presence of iodide ions is probably due to the change of metal/iodide adsorption from a state of physisorption to chemisorption as proposed by Feller *et al*[15].

Mikhailova *et al*[16] have shown that the adsorption of 'onium' type of compounds in sulphuric acid in presence of halides on nickel increases from chloride, bromide to iodide and the increase in overpotential is up to 65-75 mv in presence of iodide ions. According to Hackerman *et al*[6] the adsorption of organic materials is not always a direct combination of organic molecules with the metal surface itself but that in some cases adsorption of inhibitors takes place through already adsorbed halide or sulphate ions. Thus, the nitrogen containing organic compounds used in the present investigation, though, remaining as organic cations in solution, influence the cathodic partial process synergistically. All the organic compounds increase the overpotential in presence of iodide ion and thus supporting the above views.

Thus the synergistic behaviour of the organic compounds, on nickel in 1*N* sulphuric acid, in presence of halides may be interpreted due to the co-adsorption of the halide ions and the organic cationic compounds, though at higher cathodic potentials role of halide ions adsorption decreases due to their desorption from the electrode surface.

Acknowledgement

The authors thank the University Grants Commission (India) for financing the research project.

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Synthesis and Biological Activity of New Insecticides, Part I*

Synthesis of N-(-2-Mercapto acetyl-5-aryl-amino, 1,3,4 Thiadiazolyl) Ureas and N'-(S-acetyl-N-aryl Dithiocarbamoyl)-N³-Aryl Ureas

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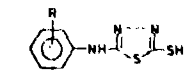
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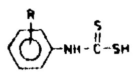
Manuscript received 10 July 1979, revised 13 March 1980, accepted 27 May 1980

TWENTY new urea derivatives have been synthesized by the condensation of chloroacetyl urea with several 2-mercapto-5-arylamino-1,3,4 thiadiazole and sodium salt of N-aryl dithiocarbamate. All the compounds were tested for their insecticidal activity.

The chemistry and wide range of pesticidal[1-3] properties of urea derivatives have been cited in the literature. A number of thiadiazole compounds were reported as insecticides[3], fungicides[4] and bactericides. The insecticidal properties of condensation products of chloroacetyl urea with sodium salt of N-aryl-dithiocarbamate were reported[5]. With a view to study the insecticidal activity we synthesized several compounds by condensing chloroacetyl urea, with several 2-mercapto 5-arylamino-1, 3, 4 thiadiazoles and sodium salt of N-aryl dithiocarbamic acids.

In all twenty compounds have been synthesized by replacing the active hydrogen of I and II by chloroacetyl urea.


(I)


(II)

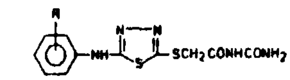
Experimental

Chloroacetyl urea was prepared according to the method of Hoegberg *et al*[6]. Chloroacetyl ureas were prepared by following the method of Jacobs *et al*[7]. 2-Mercapto-5-arylamino-1, 3, 4 thiadiazoles have been synthesized by reported methods[8-9]. Sodium salt of N-aryl dithiocarbamic acid was prepared by usual methods.

N-(-2 Mercapto acetyl-5-arylamino-1, 3, 4 thiadiazolyl) Urea :

A mixture of corresponding 2-mercapto-5-arylamino thiadiazole (0.01 mole) and chloroacetyl urea (0.01 mole) was refluxed in methanol for three hours under stirring in the presence of sodium hydroxide (0.01 mole). The reaction mixture was filtered, solvent removed under reduced pressure and solid obtained was recrystallised from ethanol. The analysis and m.p.s are recorded in Table 1.

TABLE 1

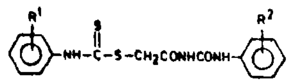


Sl. No.	R	M.P. °C	Yield	Molecula formula	%of N Found	Calc.
1.	H	210	61	$C_{11}H_{11}N_5O_2S_2$	22 46	22.65
2.	2-CH_3	208	60	$C_{12}H_{13}N_5O_2S_2$	21.78	21.36
3.	3-CH_3	199	62	$C_{12}H_{13}N_5O_2S_2$	21.12	21.36
4.	4-CH_3	210	68	$C_{12}H_{13}N_5O_2S_2$	21.34	21.36
5.	2-OCH_3	190	68	$C_{12}H_{13}N_5O_3S_2$	21.00	20.64
6.	4-OCH_3	197	66	$C_{12}H_{13}N_5O_3S_2$	20.98	20.64
7.	2-OC_2H_5	215	70	$C_{13}H_{15}N_5O_3S_2$	19.46	19.83
8.	3-Chloro	203	64	$C_{11}H_{10}N_5O_2S_2Cl$	20.62	20.40
9.	4-Chloro	235	69	$C_{11}H_{10}N_5O_2S_2Cl$	20.58	20.40

N¹-(S-acetyl-N-aryl dithiocarbamoyl)-N³-aryl urea :

A mixture of the corresponding chloroacetyl aryl urea (0.01 mole) and sodium salt of N-aryl dithiocarbamic acid (0.01 mole) in dry acetone was refluxed for two hours under stirring. The reaction mixture was filtered and the solvent was removed under reduced pressure. Solid obtained was recrystallised from ethyl alcohol/acetone. M.ps. and analytical data are recorded in Table 2.

TABLE 2



Sl. No.	R¹	R²	M.P. °C	Yield	Molecular formula	%of N Found	Calc.
10.	H	4-Br	134-35	70	$C_{16}H_{14}N_3O_2S_2Br$	9.78	9.90
11.	2-CH_3	3-Cl	140-41	67	$C_{17}H_{16}N_3O_2S_2Cl$	10.98	10.66
12.	2-CH_3	4-Br	130	83	$C_{17}H_{16}N_3O_2S_2Br$	9.39	9.58
13.	3-CH_3	3-Cl	145-47	73	$C_{17}H_{16}N_3O_2S_2Cl$	10.91	10.66
14.	4-CH_3	3-Cl	152	68	$C_{17}H_{16}N_3O_2S_2Cl$	10.95	10.66
15.	2-OCH_3	3-Cl	118	78	$C_{17}H_{16}N_3O_3S_2Cl$	9.95	10.24
16	2-OCH_3	4-Br	131	64	$C_{17}H_{16}N_3O_3S_2Br$	9.42	9.25
17.	4-OCH_3	3-Cl	133	81	$C_{17}H_{16}N_3O_3S_2Cl$	9.95	10.24
18.	4 OCH_3	4-Br	135	67	$C_{17}H_{16}N_3O_3S_2Br$	9.41	9.25
19.	4-Cl	3-Cl	135	75	$C_{16}H_{13}N_3O_2S_2Cl_2$	10.40	10.12
20.	4-Cl	4-Br	140	80	$C_{16}H_{13}N_3O_2S_2ClBr$	8.89	9.15

All the melting points were taken in open capillary tubes and are uncorrected.

Determination of Insecticidal Activity :

The method of Joshi *et al*[10] was used to determine the insecticidal activity against adult male and female cockroaches (*Periplanata americana*). Compounds were dissolved in acetone and used at a conc. of 0.1% and 0.5%. The activity of the compounds were compared with well known insecticide,

* Accepted for oral presentation to the Annual Convention of Chemists of Indian Chemical Society, Calcutta.

ethyl parathion. In a concentration of 0.1% and 0.5% the mean K. D. (knock down) Time (h) of ethyl parathion is 4.5 and 5.5 respectively. All the compounds were tested but the compounds No. 8, 10, 12, 17, 19 and 20 exhibited appreciable insecticidal activity.

Acknowledgement

One of the authors (R.S.S.) is grateful to U.P.S. C.S.T., Lucknow for the award of a Research Assistantship.

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Preparation and Fungitoxicity of Substituted Sulphamidophenyl-*O*-Alkyl Xanthates

PREM DUREJA*

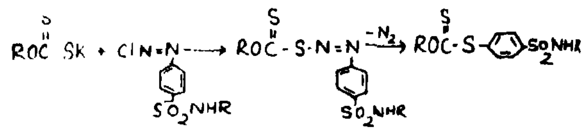
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Manuscript received 3 May 1979, revised 14 September 1979, accepted 27 May 1980

THIRTY two substituted sulphamidophenyl-*O*-alkyl xanthates have been prepared and evaluated *in vitro* against *Alternaria tenuis* and *Helminthosporium sativum*. A relation between fungitoxicity and structure has also been established.

A large number of salt of *O*-alkyl derivatives of xanthates have been reported in recent years to possess fungicidal activity against conidia of *M. fructicola*[1,2]. The potassium xanthates up to C_8 were tested for toxicity in mice and Tubifex-tubifex worm[3]. They have also been used in the concentration of ores[4] and cosmetics[5]. A perusal of literature on xanthates revealed that mostly they have been used as metallic salts with very little emphasis on the esters. Benzyl butyl xanthate is used as an insecticide for red spider[6]. Earlier some halogenonitrophenyl esters of -*O*-methyl and -*O*-ethyl xanthates were found to be toxic[7].

This paper deals with the synthesis of substituted sulphamidophenyl-*O*-alkyl xanthates with efficacy results and structure-activity relationship. They have been prepared by the condensation of potassium salt of -*O*-alkyl xanthate(I) and diazotised sulphanilamide(II) in aqueous solution at 0-15°. The intermediate diazo derivative(III) loses nitrogen and is converted into the corresponding substituted sulphamidophenyl-*O*-alkyl xanthate(IV).



I II III IV

Experimental

Potassium salt of -O-alkyl xanthate : Prepared according to the method given in the literature[8].

O-alkyl-substituted Sulphamidophenyl Xanthate : Substituted sulphanilamide (0.01*M*) dissolved in concentrated hydrochloric acid (10 ml) was diluted with water (40 ml). The resulting solution was cooled to 0° and treated with a solution of sodium nitrite (0.01*M*) dissolved in water (10 ml). The solution of diazonium salt of sulphanilamide so obtained was then added dropwise to a well cooled solution of potassium-*O*-alkyl xanthate (0.01 *M*). The stirring was continued for half an hour. The solution was then heated on a water bath till the evolution of nitrogen ceased. On cooling, substituted sulphamidophenyl-*O*-alkyl xanthates separated out. These were filtered and crystallised from methyl alcohol. The physical data of these compounds are given in Table 1 alongwith their fungitoxicity.

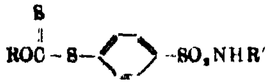
Fungitoxicity of substituted sulphamidophenyl-O-alkyl xanthates :

These compounds were tested for their antifungal activity against *Alternaria tenuis* and *Helminthosporium sativum* by spore germination method[9]. Ed_{50} values were determined from data for five con-

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centrations of the test compounds on a log probit scale. The results are given in Table 1.

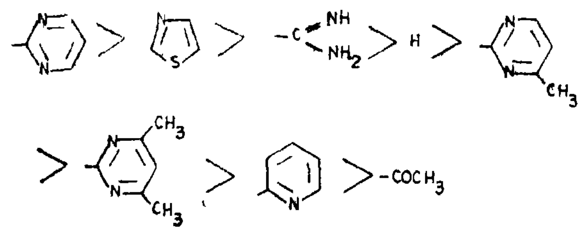
TABLE 1—PHYSICAL DATA AND FUNGITOXICITY OF SUBSTITUTED SULPHAMIDOPHENYL-*O*-ALKYL XANTHATES



Compound	R	R'	M.P.(°C)	10^6ED$_{50}$(M)
1.	CH_3	H	182	164.0
2.	,,	-acetyl	120	420.0
3.	,,	-2-thiazolyl	176	33.0
4.	,,	-2-pyridyl	157	210.0
5.	,,	-2-pyrimidyl	187	30 0
6.	,,	-2-(4-methyl) pyrimidyl	150	200.0
7.	,,	2-(4,6-dimethyl)-pyrimidyl	132	200.0
8.	,,	-2-guanidyl	95	37.0
9.	C_2H_5	– H	180	170.0
10.	,,	– $COCH_3$	69	549.0
11.	,,	-2-thiazolyl	162	37.0
12.	,,	-2-pyridyl	94	250.0
13.	,,	-2-pyrimidyl	223	33.0
14.	,,	-2-(4-methyl) pyrimidyl	198	210.0
15.	,,	-2-(4-6-dimethyl)-pyrimidyl	205	240.0
16.	,,	-2-guanidyl	140	56.0
17.	C_3H_7	– H	219	200.0
18.	,,	-acetyl	182	575.0
19.	,,	-2-thiazolyl	159	63.0
20.	,,	-2 pyridyl	139	290.0
21.	,,	-2-pyrimidyl	147	55.0
22.	,,	-2-(4-methyl)-pyrimidyl	181	420.0
23.	,,	2-(2,6-dimethyl)-pyrimidyl	202	450.0
24.	,,	-2-guanidyl	120	72.0
25.	C_4H_9	– H	139	210.0
26.	,,	-acetyl	90	610.0
27.	,,	-2-thiazolyl	176	64.0
28.	,,	-2-pyridyl	96	300.0
29.	,,	-2-pyrimidyl	209	63.0
30.	,,	-2-(4-methyl)-pyrimidyl	215	450.0
31.	,,	-2-(4,6-dimethyl-pyrimidyl)	219	575.0
32.	,,	-2 guan'dyl	100	80.0

Results and Discussion

Structure-Activity Relationship : From Ed$_{50}$ value (Table 1), the most active compound of this series was found to be 2-pyrimidyl sulphamidophenyl-*O*-methyl xanthate (compound No. 5) which is followed by -2-thiazolyl (No. 3). It appears that substitution of sulphamidophenyl by -2-acetyl, -2-pyridyl, 2-(4-methyl pyrimidyl) and -2-(4, 6-dimethyl-pyrimidyl) reduces the activity. In fact -2-thiazolyl, -2-pyrimidyl and -2-guanidyl sulphamidophenyl-*O*-alkyl xanthates are the only promising fungitoxicants in this class of compound. The above observation is confirmed from Table 1. This is evident from the following order of activity :



The 2-acetyl substituted compound is totally inactive.

In the -*O*-alkyl moiety the presence of lower alkyl group generally increases the fungitoxicity. Thus it has been seen that there is slight fall in the activity when methyl group is replaced by ethyl group, but there is a sharp fall in the activity when replaced by propyl and butyl groups. Table 1 shows that the order of fungitoxicity is as given below :

$$CH_3 > C_2H_5 > C_3H_7 > C_4H_9 >$$

Acknowledgement

The author is thankful to Dr. S. P. Gupta, Principal, D. N. College, Meerut. Thanks are due to Dr. R. S. Kapil, C.D.R.I., Lucknow for spectral and C, H analysis.

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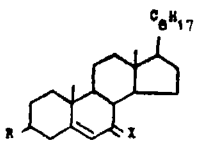
A Method of Deoximation Reaction of Lead(IV) Acetate with ∝, β-Unsaturated Steroidal Ketoximes

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Manuscript received 8 June 1979, revised 20 March 1980, accepted 27 May 1980

YUKAWA and coworkers[1] reported deoximation of a number of keto and aldoximes in acetic acid with lead(IV) acetate. To the best of our knowledge deoximation of ∝, β-unsaturated steroidal oximes with this reagent is not reported. The present note deals with the reaction of $Pb(OAc)_4$ with 3β-acetoxycholest-5-en-7-one oxime(I)[2] and its 3β-chloro analogue(II)[3].



	R	X
(I)	OAc	NOH
(II)	Cl	NOH
(III)	OAc	O
(IV)	Cl	O

The reaction of oximes(I) and (II) in dry benzene with $Pb(OAc)_4$ provided invariably 3β-acetoxycholest-5-en-7-one[4](III) and 3β-chloroketone[5](IV) respectively in excellent yield, thus giving an easy method for purification of such compounds in multistep synthesis of steroidal compounds.

Experimental

Melting points are uncorrected. I.R. spectra were recorded with a Perkin-Elmer 237 spectrophotometer in Nujol. N.M.R. spectra were run in $CdCl_3$ with A60 Varian instrument with TMS as the internal standard. Ultraviolet spectra were determined in 95% ethanol with an Unicam Sp 800 spectrophotometer. (s, singlet ; br, broad ; $W_{\frac{1}{2}}$, half band width).

Reaction of 3β-acetoxycholest-5-en-7-one oxime(I) with lead(IV) acetate :

The oxime(I) (2.0 g) dissolved in dry benzene (100 ml) was treated with lead tetra acetate (4.0 g). The reaction mixture was refluxed for 10 hrs. The solvent was removed under pressure and oil thus obtained was chromatographed over silica gel (ca. 40 g). Elution with pet. ether-ether (15 : 5) provided the ketone(III) which was crystallized from pet. ether (1.68 g), m.p. 161-163° (reported[4] m.p. 164°).

U. V. : λ_{max} 238 nm

I. R. : ν_{max} 1730 ($CH_3-\overset{O}{\overset{\|}{C}}-O$), 1670 ($-C=C-\overset{O}{\overset{\|}{C}}-$), 1630 ($-C=C-$), 1240 cm^{-1} ($-\overset{O}{\overset{\|}{C}}-O-$).

N.M.R. : δ 5.6 s (C_6-H), 4.65 br ($C_3-\alpha H$; $W_{\frac{1}{2}}=16$ Hz ; axial)[6], 1.98 s ($C_3\beta-O-\overset{O}{\overset{\|}{C}}-CH_3$), 1.22 s ($C_{10}-CH_3$), 0.67 ($C_{18}-CH_3$), 0.83 and 0.89 (other methyl protons).

Reaction of 3β-chlorocholest-5-en-7-one oxime(II) with lead(IV) acetate :

The oxime (II) under identical reaction conditions (same amounts of reactants were used) provided ketone (IV), (1.73 g), m.p. 144 – 145° (reported[5] m.p. 144 – 145°).

U. V. : λ_{max} 243 nm

I.R. : ν_{max} 1675 ($-C=C-\overset{O}{\overset{\|}{C}}-$), 1635 ($-C=C-$), 768 cm^{-1} ($C-Cl$).

N.M.R. : δ 5.38 s (C_6-H), 3.86 br ($C_3\ \alpha-H$; $W_{\frac{1}{2}}=20$ Hz; axial), 1.25 s ($C_{10}-CH_3$), 0.70 ($C_{18}-CH_3$), 0.83 and 0.93 (other methyl protons).

Acknowledgement

We are thankful to Prof. W. Rahman and Prof. M. S. Ahmad for necessary facilities and helpful discussion. Financial assistance to (H. A. and S. Z.) from CSIR (New Delhi) is gratefully acknowledged.

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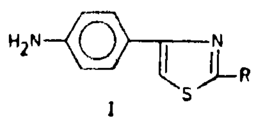
J. Indian Chem. Soc.,
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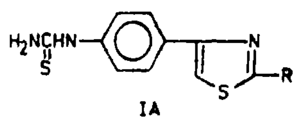
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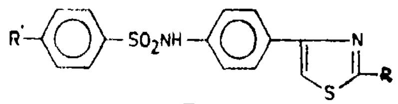
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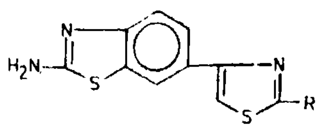
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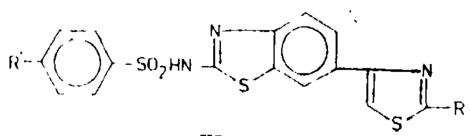
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II



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IV

AUTHOR INDEX

J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 861-863

Studies on the Complexes of Fe(III), Co(III), Ni(II) and Cu(II) with Potassium *n*-Butyl Xanthate

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Manuscript received 7 April 1979, revised 15 February 1980, accepted 9 July 1980

The reaction of several transitional metals with potassium *n*-butyl xanthate was studied by electrometric titrations and chemical analysis. The 1 : 2 complexes were formed with Fe(III), Ni(II) and Cu(II) and a 1 : 3 complex in the case of Co(II). These complexes were subjected to spectral and magnetic studies in order to determine their structural characteristics. The magnetic moment studies provide evidence for the existence of an octahedral high spin xanthate complex in the case of Fe(III), an octahedral cobalt complex with cobalt in (III) oxidation state and Cu(II) and Ni(II) square planar complexes. Infrared spectra show that C–O–C– is not involved in complex formation. On the other hand coordination with sulphur takes place as evinced by the shift in the C=S stretching bands. In case of Fe(III) complex there is evidence of H_2O being in the coordination sphere.

IN comparison to other sulphur containing ligands, reaction of xanthates with metals have not been systematically studied. Metal xanthates are quite important as insecticides and fungicides, and they have found use in analytical separations. Comprehensive investigation on their composition and structural characteristics is therefore, very desirable.

Earlier studies were mostly limited to the elucidation of crystal parameters of nickel, cobalt and ferric ethyl xanthates. Physico-chemical studies on these complexes are of recent origin. Claudia and co-workers[1] have reported results of spectral studies on ferric potassium xanthates. Analytical studies were carried out by Rolando *et al*[2] for the separation of Ni(II), Co(II) ethyl xanthate complexes from zinc solution by solvent extraction technique and by Wilms *et al*[3] for the micro determination of cobalt by potassium methyl xanthate.

The survey of the literature has shown that higher homologues of alkyl xanthates have not so far been used as ligands. It was therefore, thought worthwhile to carry out physico-chemical studies on the reactions of potassium *n*-butyl xanthate (henceforth abbreviated as PNBX) with some transitional metals. The results of these investigations are reported in this paper.

Experimental

Potassium *n*-butyl xanthate (PNBX) was prepared[4] from *n*-butyl alcohol, carbon disulphide and KOH. The product was recrystallised from ethanol and petroleum ether (Found S = 33.9%, calc. 34.0). The compound was characterised by i.r.

Air free double distilled conductivity water was used for preparing solutions throughout the experiments. Freshly prepared PNBX solution was always used. Stock solutions of nickel sulphate, cobalt chloride, ferric chloride and copper acetate were prepared by dissolving the B.D.H. 'AR' grade salt in conductivity water. Their strengths were determined by the usual methods.

Both direct and reverse conductometric titrations were performed to decide the composition of the metal Fe(III), Co(II), Ni(II), Cu(II)-*n*-butyl xanthato-complexes. Phillips conductivity bridge with a dip type conductivity cell (cell constant 0.62) was used for conductance measurements.

Amperometric titrations were performed to confirm metal-ligand ratio using Toshniwal manual polarograph. Potassium chloride solution (2 *M*) was used as the supporting electrolyte and freshly prepared 0.2% solution of gelatin was used as maximum suppressor in all the cases. A constant potential of – 0.3 volts vs SCE was selected from the plateau of PNBX for all the titrations except in case of Cu(II) where a potential of –0.1 V vs SCE was applied.

The following method was used for the isolation of the complexes :

250 ml of $1.0 \times 10^{-2} M$ of metal salts solutions were added to 500 ml of equimolecular solution of PNBX while for Co(II), the two solutions were mixed in the molar ratio 1 : 3. The dark brown, dark yellow, pale yellow and dark green xanthato-complexes of the respective metals got precipitated

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TABLE 1—ANALYTICAL RESULTS

Complex	% of metal Found	% of metal Requires	% of sulphur Found	% of sulphur Requires	% of Chlorine Found	% of Chlorine Requires
$[(ROCS_2)_2Cl.H_2O\ Fe]$	13.6	13.7	30.6	31.4	8.7	8.7
$[(ROCS_2)_3Co]$	11.6	11.6	37.9	37.9	—	—
$[(ROCS_2)_2Ni]$	16.4	16.4	35.8	35.8	—	—
$[(ROCS_2)_2Cu]$	17.5	17.5	35.4	35.4	—	—

R→$CH_3(CH_2)_8$

TABLE 2—MAGNETIC MEASUREMENTS

Complex	Temp. K°	$X_M \times 10^{-6}$ c.g.s. units	μ_{eff} Found	(B.M.) Calc.	n	Hybridization	Stereo-Chemistry
$[(ROCS_2)_2Cl.H_2O\ Fe]$	302	14894	5.99	5.92	5	Sp^3d^2	High spin octahedral
$[(ROCS_2)_3Co]$	302	Diamagnetic	0	0	0	d^2Sp^3	Low spin octahedral
$[(ROCS_2)_2Ni]$	302	Diamagnetic	0	0	0	dSp^2	Square planar
$[(ROCS_2)_2Cu]$	302	10717	1.69	1.73	1	dSp^2	Square planar

n = number of unpaired electrons.

TABLE 3—INFRARED FREQUENCIES (cm^{-1}) AND THEIR ASSIGNMENTS

Absorption bands (cm^{-1})

PNBX	$[(ROCS_2)_2Cl.H_2O\ Fe]$	$[(ROCS_2)_3Co]$	$[(ROCS_2)_2Ni]$	$[(ROCS_2)_2Cu]$	Assignments
1060(s)	1020(s)	1040(s)	1028(s)	1030(s)	C = S (sulphur is involved)
1090(s)	1120(s)	1125(m)	1120(s)	1118(s)	C – O – C (oxygen is not involved)
1160(s)	1216(s)	1200(sb)	1215(m)	1190(s)	
—	1630(sb), 3300-3200(sb).	—	—	—	H_2O present

s = sharp, m = medium, sb = sharp broad.

from the resulting solutions. These were kept overnight, filtered and dried on filter papers. The solid products were then recrystallised with benzene [Fe(III), Ni(II), Co(II)-complexes] and with acetone [Cu-complex], under reduced pressure, and dried in vacuum desiccator. The isolated complexes were subjected to chemical analysis for metal and sulphur. The iron complex was also analysed for chloride ion. The results are given in Table 1.

The magnetic susceptibility measurements were carried out with the help of Gouy's magnetic balance having a semimicrometer balance, model C Meltlov Zoric type H_{16} No. 140050 at 29°. The observed molar susceptibilities were corrected for diamagnetic contributions. The results are given in Table 2.

Infrared spectrum of Fe(III), Co(III), Ni(II) and Cu(II) complexes of PNBX were taken in KBr medium by the method of fast scanning using 'Beckman I.R. 20'. The principal assignments for respective metal complexes and ligand are given in Table 3.

Results and Discussion

Conductometric titrations show sharp breaks corresponding to the metal : ligand ratios of 1 : 2 for Fe(III), Ni(II) and Cu(II) and 1 : 3 for Co(III). The ratios are further supported by the results of the amperometric titrations which were carried out on the plateau of PNBX which gave an anodic wave. These results were confirmed by the results of chemical analysis (Table 1).

The results of the magnetic measurements presented in Table 2 throw light on the stereo-chemistry of these complexes. The magnetic moment for the Fe(III) complex, $[Fe(ROCS)_2)_2Cl(H_2O)]$ was found to be 5.99 B.M. which is in fair agreement for high spin (sp^3d^2) octahedral Fe(III) complexes[5,6].

The cobalt complex, $[Co(ROCS_2)_3]$ was found to be diamagnetic which is in agreement with the behaviour exhibited by low spin (d^2sp^3) cobalt(III) complexes[7-9]. This also indicates that Co(II) changes to Co(III) during complexation. Ligands containing the CS_2^- moiety are known to form stable Co(III) complexes and generally the Co(II) complexes, if formed, are difficult to isolate.

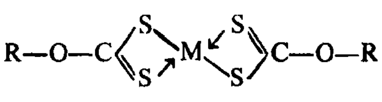
The Ni(II) complex, $[Ni(ROCS_2)_2]$ was found to be diamagnetic while the Cu(II) complex, $[Cu(ROCS_2)_2)]$ showed a magnetic moment of 1.69 B.M. corresponding to one unpaired spin. This indicates a square planar configuration[10,11] (dsp^2) for both the Ni(II) and Cu(II) complexes.

In the infrared spectrum of PNBX, the C–O–C absorption bands appeared at 1090 cm^{-1} and 1160 cm^{-1}, whereas in *n*-butyl xanthato-complexes of Fe(III), Co(II), Ni(II) and Cu(II), the C–O–C absorption bands were observed at 1120 cm^{-1} and 1216 cm^{-1} ; 1125 cm^{-1} and 1200 cm^{-1} ; 1120 cm^{-1} and 1215 cm^{-1} ; 1118 cm^{-1} and 1190 cm^{-1} ; respectively. These observations were in accord with the findings of Little *et al*[12] who had shown that in xanthato-complexes, the C–O–C stretching frequencies appeared in the region 1110-1140 cm^{-1} and 1200 cm^{-1} whereas the frequency of C–O–C band in alkyl xanthates were observed in the lower region. The observations under discussion indicated non-participation of oxygen of C–O–C in bonding with metals.

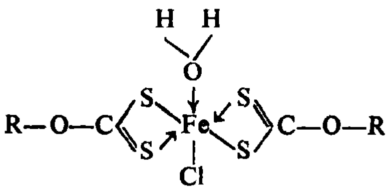
In the infrared spectrum of potassium *n*-butyl xanthate the C=S stretching frequency band appeared at 1060 cm^{-1}. Little *et al* (loc cit.) had reported that in xanthato-complexes the C=S stretching band appeared at 1020-1070 cm^{-1}. In the i.r. spectra of Fe(III), Co(II), Ni(II) and Cu(II) complexes with PNBX, the C=S stretching band appeared at 1020 cm^{-1}, 1040 cm^{-1}, 1028 cm^{-1} and 1030 cm^{-1}, respectively. The lowering of the frequency of C=S band in *n*-butyl xanthato-complexes indicated involvement of sulphur in bonding with the metals.

Furthermore in the i.r. spectrum of Fe(III)-PNBX complex, the appearance of a broad absorption band in the region 3500-3200 cm^{-1} and a sharp band at 1630 cm^{-1}, was a strong evidence for the presence of water molecule in the complex.

On the basis of spectral, magnetic and other studies the following structures could be assigned to these metal complexes



(M–NBX)
M=Ni(II) & Cu(II)



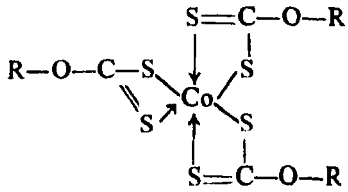
[Fe(III)-NBX]

Structure and Mechanism for Co(III) Complex Formation :

Ordinarily the Co(II) complex should also give the metal-ligand stoichiometric ratio of 1 : 2. But since the physical methods, chemical analysis and magnetic measurement, all provided evidence for the Co(III) complex, it might be inferred that the complex formation was accompanied by simultaneous oxidation of the unstable reaction product. As such the following steps could be written for the reaction :

$$CoCl_2 + 2ROCS_2K \longrightarrow (ROCS_2)_2Co + 2KCl$$

$$4(ROCS_2)_2Co + O_2 + 2H_2O + 4(ROCS_2K) \longrightarrow 4(ROCS_2)_3Co + 4KOH$$



(Co–NBX)

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 864-867

2-Methylpentane-2,4-Dioxysilicon(IV) Complexes of 4-(Alkyl or Aryl)Amino-3-Pentene-2-One

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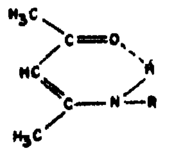
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Manuscript received 19 September 1978, revised 2 May 1980, accepted 9 July 1980

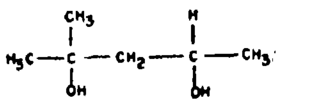
2-Methylpentane-2,4-dioxysilicon(IV) complexes of the type $Si(SB)_2(C_6H_{12}O_2)$ (where SBH and $C_6H_{14}O_2$ represent the monofunctional bidentate Schiff base and 2-methylpentane-2,4-diol molecules respectively) have been synthesized by the reactions of silicon tetraacetate, monofunctional bidentate Schiff base and 2-methylpentane-2,4-diol in 1 : 2 : 1 molar ratio. The resulting derivatives are non-electrolytes in DMF and monomers in boiling benzene. On the basis of infrared and ^1H NMR spectral studies, suitable structures have been indicated for the resulting new compounds.

A careful survey of the literature revealed that except for a few publications on the β-ketoamine derivatives of silicon with tridentate[1,2] ligands, systematic studies on other types of β-ketoamine derivatives are lacking. It was, therefore, considered of interest to synthesize some new silicon derivatives of bidentate β-ketoamines and to study their main characteristics.

In previous communications[3,4] from these laboratories, silicon complexes with the Schiff bases derived from β-diketones and aminoalcohols have been reported. In this paper, the reactions of silicon tetraacetate with the Schiff bases derived from 2, 4-pentanedione and alkyl or arylamines have been discussed. The monofunctional bidentate Schiff bases, and 2-methylpentane-2, 4-diol used in the present investigations may be represented by the general structures (I) and (II)



(I)



(II)

(where R = $-C_2H_5$, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, sec-C_4H_9, $tert$-C_4H_9, $-C_6H_5$, o-ClC_6H_4, o-$OCH_3C_6H_4$ and p-$CH_3C_6H_4$).

Experimental

All the reactions have been carried out under strictly anhydrous conditions. The starting materials were prepared as reported earlier.[4]

Preparation of β-ketoamines :

The β-ketoamines were prepared by taking equimolar amounts of 2, 4-pentanedione and amines in benzene and refluxing for 4-5 hours. The water formed in the reaction was removed azeotropically with benzene and the resulting products were distilled before use. Their melting or boiling points are as follows :

1. 4-(Ethyl)amino-3-pentene-2-one ($C_7H_{13}NO$), b. p. 165°/7.5 mm.

2. 4-(n-Propyl)amino-3-pentene-2-one ($C_8H_{15}NO$), b. p. 77°/0.05 mm.

3. 4-(iso-Propyl)amino-3-pentene-2-one ($C_8H_{15}NO$)*. b. p. 85°/3.0 mm.

4. 4-(n-Butyl)amino-3-pentene-2-one ($C_9H_{17}NO$), b. p. 68°/0.3 mm.

5. 4-(sec-Butyl)amino-3-pentene-2-one ($C_9H_{17}NO$)*, b. p. 62°/0.01 mm.

6. 4-(iso-Butyl)amino-3-pentene-2-one ($C_9H_{17}NO$)**, b. p. 82°/0.05 mm.

7. 4-($tert$-Butyl)amino-3-pentene-2-one ($C_9H_{17}NO$)*. b. p. 127°/7.1-7.2 mm.

8. 4-(Phenyl)amino-3-pentene-2-one ($C_{11}H_{13}NO$), b. p. 97°/0.2 mm.

9. 4-(o-Chlorophenyl)amino-3-pentene-2-one ($C_{11}H_{12}NOCl$), b. p. 140°/2.0 mm.

10. 4-(o-Methoxyphenyl)amino-3-pentene-2-one ($C_{12}H_{15}NO_2$), b. p. 128-129°/0.7-0.8 mm.

11. 4-(p-Methylphenyl)amino-3-pentene-2-one ($C_{12}H_{15}NO$), m. p. 58°.

Analytical Methods and Physical Measurements :

Infrared spectra were recorded in the range, 4000-400 cm^{-1} with a Perkin-Elmer 557 grating IR

TABLE 1—REACTIONS OF SILICON TETRAACETATE WITH SCHIFF BASES AND 2-METHYLPENTANE-2,4-DIOL ($C_6H_{14}O_2$) IN 1 : 2 : 1 MOLAR RATIO

Sl. No.	$Si(OAc)_4$ (g)	Schiff base (g)	$C_6H_{14}O_2$ (g)	Refluxing time (hrs)	Product, yield (g) and characteristics	Acetic acid in the azeotrope (g) Found (Calcd)	Analysis(%) Si Found (Calcd)	Analysis(%) N Found (Calcd)	Mol. Wt. Found (Calcd)
1.	1.55	$C_7H_{13}NO$ (1.49)	0.69	14	$Si(C_6H_{12}O_2)(C_7H_{12}NO)_2$, (2.01), yellow viscous liquid, soluble in benzene	1.39 (1.40)	7.02 (7.07)	7.20 (7.06)	410 (396)
2.	1.05	$C_8H_{15}NO$ (1.12)	0.47	16	$Si(C_6H_{12}O_2)(C_8H_{14}NO)_2$, (1.50), brown semi-solid, soluble in benzene	0.94 (0.95)	6.60 (6.61)	6.60 (6.59)	430 (424)
3.	1.37	$C_8H_{15}NO$* (1.46)	0.61	17	$Si(C_6H_{12}O_2)(C_8H_{14}NO)_2$*, (1.98), yellow semi-solid, soluble in benzene	1.01 (1.24)	6.75 (6.61)	6.50 (6.59)	432 (424)
4.	1.28	$C_9H_{17}NO$ (1.50)	0.57	15	$Si(C_6H_{12}O_2)(C_9H_{16}NO)_2$, (1.88), yellow solid, soluble in benzene	1.09 (1.16)	6.40 (6.20)	6.21 (6.18)	441 (452)
5.	2.00	$C_9H_{17}NO$* (2.35)	0.89	16	$Si(C_6H_{12}O_2)(C_9H_{16}NO)_2$*, (3.01), brown semi-solid, soluble in benzene	1.80 (1.81)	6.34 (6.20)	6.20 (6.18)	450 (452)
6.	1.98	$C_9H_{17}NO$** (2.32)	0.88	18	$Si(C_6H_{12}O_2)(C_9H_{16}NO)_2$**, (2.99), yellow semi-solid, soluble in benzene	1.79 (1.80)	6.22 (6.20)	6.30 (6.18)	457 (452)
7.	0.97	$C_9H_{17}NO$# (1.14)	0.45	15	$Si(C_6H_{12}O_2)(C_9H_{16}NO)_2$#, (1.57), brownish yellow semi-solid, soluble in benzene	0.78 (0.88)	6.54 (6.20)	6.09 (6.18)	472 (452)
8.	1 50	$C_{11}H_{13}NO$ (1.99)	0.61	20	$Si(C_6H_{12}O_2)(C_{11}H_{12}NO)_2$, (2.40), yellow solid, soluble in benzene	1.20 (1.36)	5.71 (5.69)	5.59 (5.68)	482 (492)
9.	1.43	$C_{11}H_{12}NClO$ (2.27)	0.63	18	$Si(C_6H_{12}O_2)(C_{11}H_{11}NClO)_2$, (2.84), yellow solid, soluble in benzene	1.30 (1.30)	5.22 (5.00)	5.01 (4.98)	581 (561)
10.	1.73	$C_{12}H_{15}NO_2$ (2.68)	0.77	22	$Si(C_6H_{12}O_2)(C_{12}H_{14}NO_2)_2$, (3.20), yellow semi-solid, soluble in benzene	1.55 (1.57)	5.19 (5.07)	4.99 (5.05)	568 (552)
11.	1.46	$C_{12}H_{15}NO$ (2.09)	0.65	20	$Si(C_6H_{12}O_2)(C_{12}H_{14}NO)_2$, (2.67), yellow solid, soluble in benzene	1.28 (1.32)	5.28 (5.39)	5.45 (5.37)	529 (520)

*, ** and # have been used to distinguish between the compounds of the same molecular formula.

Spectrophotometer as nujol mulls and in some cases as neat liquids. The molecular weights were determined in boiling benzene by means of an ebulliometer (Gallen Kamp) using thermistor sensing. Conductivity measurements were carried out by a conductivity bridge type 235 and the ^1H NMR spectra were recorded in benzene with the help of Perkin-Elmer RB-12 Spectrometer using TMS as the internal standard.

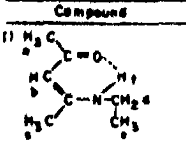
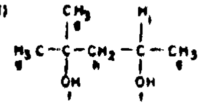
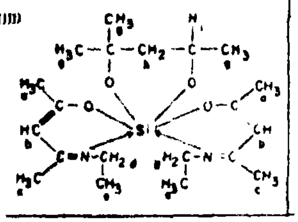
Synthesis of Silicon(IV) β-ketoamine Complexes :

On treating silicon tetraacetate with the ligands, SBH and $C_6H_{14}O_2$ in 1 : 2 : 1 molar ratios in toluene, a clear solution was obtained. The reaction mixture was refluxed at the bath temperature of ~ 130° followed by the slow fractionation of the liberated acetic acid with toluene. It was then estimated against a standard sodium hydroxide solution. The residual toluene was then removed under reduced pressure and the resulting products of the type $Si(SB)_2$ $(C_6H_{12}O_2)$ were finally dried at 50-55°/0.05 mm for 2-3 hours. The details of their analyses and syntheses are recorded in Table 1.

Results and Discussion

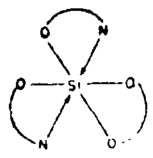
The resulting complexes are coloured liquids, semi-solids or solids and have been found to be soluble in benzene. These are quite stable in the open atmosphere and decompose on being treated with water. Attempts to distil these even under reduced pressure remained unsuccessful.

TABLE 2 — ^{1}H NMR SPECTRAL DATA OF LIGANDS AND THEIR SILICON COMPLEX IN δ(ppm)

Compound	a	b	c	d	e	f	g	h	i
(I) 	1.65	4.65	1.65	3.00	0.90	10.55	—	—	—
(II) 	—	—	—	—	—	4.80	1.30	1.90	4.05
(III) 	1.87	4.86	1.87	3.20	1.20	—	1.87++	2.50	4.30

++ merged with CH_3 marked with C.

The ebullioscopic determinations of molecular weights in boiling benzene show them to be monomers indicating a hexa-coordinated environment (III) for the central silicon atom in these derivatives.



(III)

[Where N⌒OH and HO⌒OH represent the SBH and $C_6H_{14}O_2$ molecules respectively]

Conductance :

Low molar conductance values (8-15 ohm^{-1} cm^2 mol^{-1}) for all these complexes in DMF show their non-electrolytic nature.

Infrared Spectra :

The i. r. spectra of the Schiff bases as well as their corresponding silicon complexes have been recorded. On comparing the two spectra, the following points appear to be significant from the point of view of discussion :

In the case of Schiff bases no absorption band appears in the region 3400-3200 cm^{-1}. However, on account of strong hydrogen bonding a broad band is observed in the 3050-2900 cm^{-1} region. Coordination through oxygen as well as nitrogen atoms of these groups can be inferred by the absence of any band due to νOH or νNH. This type of bonding is also substantiated by the appearance of a number of new bands of medium intensity in the region 700 - 600 cm^{-1} and these may be assigned to νSi-O.[6]

A strong band is observed in the region 1615-1595 cm^{-1} in the spectra of the Schiff bases and this is a characteristic absorption band of the azomethine group (>C=N). In the i.r. spectra of silicon complexes of Schiff bases, ν(C=N) is observed at almost the same position.

^{1}H NMR Spectral Studies :

The ^{1}HNMR spectra of 4-(ethyl)amino-3-pentene-2-one (i), 2-methylpentane-2,4-diol (ii) and their corresponding silicon complex (iii) have been recorded in benzene. The chemical shift values (δ) of the different protons are recorded in Table 2.

The comparison of the two spectra leads to the following conclusion and this is in conformity with the proposed structures of the silicon complexes :

1. The ^{1}H NMR spectra show preference for the Ketamine structure over other equilibrium forms for compound (i) as well as for the Schiff bases derived by the condensation of β-diketones with alkyl or aryl amines or diamines as reported earlier[6,7,8].

2. The 10.55 δ peak due to the hydrogen bonded NH protons of the ligand (i) disappears in compound (iii) and this indicates the chelating nature of the ligand and coordination of nitrogen to silicon.

3. The bonding of alcoholic oxygen in the compound (iii) is substantiated by the disappearance of OH proton signal which is observed at 4.80 δ in the ligand (ii).

4. The proton signals of the amine residue of the ligand moiety are shifted downfield in the spectrum of the silicon complex (iii) and this may further be due to the formation of a coordinate bond between nitrogen and silicon causing a change in the electronic environment around the above protons.

Acknowledgement

One of the authors (R. V. S.) is grateful to the C.S.I.R., New Delhi for the financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 868-870

Nature of Phenoxides of Niobium(V) and Tantalum(V)

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Manuscript received 3 January 1979, revised 6 February 1980, accepted 13 May 1980

Phenoxides of niobium(V) and tantalum(V) have been proposed to have dimeric structures on the basis of conductance, and infrared spectral studies. Lewis acid character of these phenoxides has been established by isolating compounds of composition $M(OC_6H_5)_5$.Base with nitrogenous bases. Double phenoxides of composition $M'[M(OC_6H_5)_6]$($M=Nb$ or Ta; $M'=Li$, Na or K) have also been prepared by reacting alkali metal phenoxides in 1 : 1 molar ratio which is supported by conductometric titrations in phenol.

As compared to alkoxides, very little work has been carried out on the metal phenoxides. Only scattered references are available in literature about their synthesis inspite of their utility as catalysts in many industries[1]. Kapoor and his coworkers[2] followed by Schonherr and his coworkers[3] have reported the preparation of phenoxides of niobium(V) and tantalum(V), but the structural information about these phenoxides is lacking. In the present investigations, therefore, an attempt has been made to elucidate their structure and also to explore their possibility of behaving as Lewis acid and formation of double phenoxides.

Experimental

Phenol (A.R.) was purified by crystallization from carbon tetrachloride (m.p. 43°). Phenoxides of niobium(V) and tantalum(V) viz. $Nb(OPh)_5$ (m.p. 209°); $Nb(OPh)_4Cl$ (240°); $Nb(OPh)_3Cl_2$ (234°); $Nb(OPh)_2Cl_3$ (196°); $Nb(OPh)Cl_4$ (188°); $Ta(OPh)_5$ (224°); $Ta(OPh)_4Cl$ (253°); $Ta(OPh)_3Cl_2$ (218°); $Ta(OPh)_2Cl_3$ (174°) and $Ta(OPh)Cl_4$ (157°) were prepared by the methods reported in literature[2,3] and their purity was checked by their sharp melting points and elemental analysis.

Double phenoxides of composition $M'[M(OC_6H_5)_6]$ where $M'=Li$, Na or K and $M=Nb$ or Ta, were prepared by refluxing the components in 1 : 1 molar ratio in carbon tetrachloride for 10-15 hours. The components which were individually insoluble in carbon tetrachloride went into solution on refluxing. On cooling crystalline solid separated out which was filtered, washed with carbon tetrachloride and dried under vacuum. Compounds of composition $M(OC_6H_5)_5$.Base and $MCl_4(OC_6H_5)$. Base were prepared by mixing the two components in equimolar ratio in dry carbon tetrachloride when an exothermic reaction took place. The resulting compounds were isolated by the addition of petroleum ether and dried under vacuum. But in case of compounds with pyridine N-oxide and with triphenylarsine oxide, components had to be refluxed till they went into solution and were recovered by addition of petroleum ether and dried under vacuum.

Infrared spectra of the compounds were scanned as Nujol mulls or KBr pellets on Perkin-Elmer 337 (for 400-4000 cm^{-1}) and Perkin-Elmer 621 (for 200-600 cm^{-1}).

Results and Discussion

The compounds isolated in the present studies are reported in Table 1. All these compounds are moisture sensitive but stable in dry air. They are insoluble in most of the organic solvents except slight solubility in nitrobenzene at room temperature. Molar conductance values of millimolar solution of all these compounds except double phenoxides, suggest that they are non-electrolytes while double phenoxides of composition $M'[M(OPh)_6]$ have values which indicate their ionic nature (Table 1). Information on the structure and stereochemistry of the compounds of composition $M(OC_6H_5)_5$; $MCl(OC_6H_5)_4$, $MCl_2(OC_6H_5)_3$ and $MCl_4(OC_6H_5)$ has been arrived at by their infrared spectral studies. A significant change has been observed in the spectrum of the pure ligand on complex formation. The lowering of $\nu(O-C)$ present at 1230 cm^{-1} in pure phenol by about 30-40 cm^{-1} is due to the coordination of phenolic oxygen to the metal. The bands at ~570 cm^{-1} in case of niobium compounds and at ~550 cm^{-1} in case of tantalum compounds (not present in the pure phenol) may be assigned to infrared active $(M-O)$ stretching modes. Such types of bands have been reported earlier in the same region in the case of metal alkoxides[4,5]. It is interesting to note that in these compounds no band around 900-930 cm^{-1} which could be assigned to $Nb=O$ or $Ta=O$ stretching modes[6] has been observed suggesting that no oxygen abstraction occurs in these compounds.

TABLE 1—ANALYTICAL DATA OF THE PHENOXIDES OF NIOBIUM(V) AND TANTALUM(V)

Compound	Colour	m p. (°C)	Elemental Analysis % Found M	Cl	N	% Reqd. M	Cl	N	Molar conductance ($ohm^{-1} cm^2 mole^{-1}$)
$NaNb(OC_6H_5)_6$	Light yellow	>220	12.92	—	—	13.7	—	—	7.83
$NaTa(OC_6H_5)_6$	Cream	212	24.15	—	—	23.75	—	—	6.08
$KNb(OC_6H_5)_6$	Light orange	115(d)	12.96	—	—	13.47	—	—	6.13
$KTa(OC_6H_5)_6$	Light pink	112(d)	24.37	—	—	23.20	—	—	5.62
$LiTa(OC_6H_5)_6$	Light pink	212	23.78	—	—	24.26	—	—	5.21
$Nb(OC_6H_5)_5.py$	Light yellow	159-62	14.01	—	2.14	14.59	—	2.19	1.13
$Ta(OC_6H_5)_5.py$	Light yellow	172-75	24.27	—	1.73	24.96	—	1.93	0.85
$Nb(OC_6H_5)_5.pyNO$	Light yellow	>220	13.97	—	2.01	14.24	—	2.14	1.49
$Nb(OC_6H_5)_5.Ph_3AsO$	Light brown yellow	>220	9.32 (65.01)[a]	—	4.10[b]	10.57 (65.45)[a]	—	4.54[b]	0.97
$NbCl_4(OC_6H_5).py$	Yellow	148-50	21.90	34.43	3.23	22.85	34.89	3.44	1.54
$TaCl_4(OC_6H_5).py$	Light yellow	165-67	36.14	27.98	2.52	36.56	28.68	2.82	0.93
$NbCl_4(OC_6H_5).\alpha$-pic	Light lemon yellow	135(d)	21.87	32 [illegible]0	3.13	22.09	33.73	3.32	1 46
$TaCl_4(OC_6H_5).\alpha$-pic	Golden yellow	151(d)	34.91	28.01	2.50	35.56	27.89	2.75	0.87

a = % of Carbon ; b = % of Hydrogen.

In case of compound $NbCl_4(OC_6H_5)$, an intense absorption band at 550 cm^{-1} can be attributed to ν(Nb–O) stretching mode. Since this absorption band is well below the range 570-580 cm^{-1} observed for terminal ν(Nb–O) stretching mode[4,5], this mode may be assigned to bridging Nb–O→Nb which is in agreement with the previous observations that if polymerization takes place through halogen or oxygen, then the corresponding stretching modes are observed at comparatively lower regions as compared to terminal ones[6,7].

A sharp intense band at 350 cm^{-1} assigned to ν(Nb–Cl) is observed in the compound of composition $NbCl_4(OC_6H_5)$ which is in agreement with the assignments of Djordjevic[8] and with the reported ν(Nb–Cl) vibrations for octahedral complexes[9]. Thus an octahedral disposition of chlorine and the ligand may be visualized around the metal atom for these complexes. No band which could be assigned to bridged chlorine is observed. In view of i.r. spectral studies particularly in the lower region, a dimeric structure bridging through phenoxy groups can be suggested. Similar observations have been made in case of tantalum complexes as well.

In case of complexes of composition $MCl_3(OC_6H_5)_2$, $MCl_2(OC_6H_5)_3$ and $MCl(OC_6H_5)_4$ molar conductance values of millimolar solutions in DMF (10.25-15.87 $ohm^{-1} cm^2 mole^{-1}$) suggest them to be non-ionic. Infrared spectral studies show all the important bands (Table 2) which indicate phenoxy bridging to the metal ion thereby acquiring hexa-coordination. Similar structures have been confirmed earlier also for niobium and tantalum methoxides by various workers[10,11].

TABLE 2—PRINCIPAL BANDS (cm^{-1}) OF THE PHENOXIDES OF NIOBIUM(V) AND TANTALUM(V)

Compound	ν(O–C)	ν(M–O) or (M–O+C–O)	ν(M–X)
$Nb(OPh)_5$	1196	552, 576	—
$NbCl(OPh)_4$	1198	553, 569	349
$NbCl_2(OPh)_3$	1204	540, 572	354
$NbCl_3(OPh)_2$	1198	542, 575	352
$NbCl_4(OPh)$	1201	550	350
$Ta(OPh)_5$	1190	520, 548	—
$TaCl(OPh)_4$	1196	525, 550	332
$TaCl_2(OPh)_3$	1208	521, 552	339
$TaCl_3(OPh)_2$	1200	528, 548	330
$TaCl_4(OPh)$	1201	530	335

Attempts have also been made to establish the Lewis acid character of these phenoxides by isolating some adducts with bases like pyridine, pyridine N-oxide, α-picoline and with triphenylarsine oxide (Table 1). The pure phenoxide which is dimeric through phenoxy bridging reacts with base whereby ring opening takes place. The ring opening is further ascertained from the changes which ν(Nb–O) stretching modes of the pure phenoxide experience on complexation. The band present in the lower region (540-550 cm^{-1}) attributed to bridging Nb–O→Nb in the pure compound is shifted to higher wave numbers in adducts with pyridine[12]. Further, broadening of the sharp bands in the region 570-580 cm^{-1} attributed to terminal ν(Nb–O) bond on complexation, can be due to either lowering in symmetry around the central metal or to the coordination of nitrogen of the pyridine ring with the metal because ν(M–N) vibration also occur in the region 600-400 cm^{-1} and these are always associated with the rings deformation vibrations[13]. The ν(C=N) observed at 1578 cm^{-1} for free pyridine[14-16] shifts to 1610-1620 cm^{-1} on coordination. The pyridine ring deformation vibrations

were also shifted to higher wave numbers[14]. In case of α-picoline, the bands present at 1597, 1572, 1479, 1433 and 996 cm^{-1} due to $\nu(C=C)$ and $\nu(C=N)$[17] are shifted to higher regions due to drift of electrons from nitrogen to the metal. Co-ordination of pyridine N-oxide to phenoxides is indicated by the significant lowering of $\nu(N-O)$ stretching mode from 1265 cm^{-1} to 1220-1230 cm^{-1} on complexation. The trend of shift of other characteristic bands of pyridine N-oxide arising from $\nu(C-H)$ stretching out of plane vibration of the ring and (N – O) bending mode are in the same direction as reported earlier[18]. Since there is only one band assigned to metal-chlorine stretching modes a possible *trans* structure for these adducts may be proposed[19].

Last of all, some double phenoxides of niobium and tantalum of composition $M'M(OC_6H_5)_6$ where M' = Li, Na, K and M = Nb or Ta have been prepared by refluxing the corresponding transition metal phenoxide with alkali metal phenate in 1 : 1 molar ratio in carbon tetrachloride. The stoichiometric composition has been confirmed by elemental analysis and by carrying out conductometric titrations of these solvo acids against solvo bases in phenol at $50 \pm 0.1°$. From conductance-composition curve, it can be seen that there is a sharp break at 1 : 1 molar ratio which confirms the formation of a double phenoxide as :

$$M'OC_6H_5 + M(OC_6H_5)_5 \longrightarrow M'[M(OC_6H_5)_6]$$

Similar results have already been reported by Malhotra and coworkers[20] wherein titanium(IV) phenoxides have been titrated against sodium phenate in phenol at 50°.

Acknowledgement

One of us (U. K. B.) is thankful to H. P. University, Simla for the award of a junior research fellowship. Thanks are also due to Prof. O. P. Malhotra of B. H. U., Varanasi for providing necessary facilities for infrared spectra of compounds.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 871-875

Spectral, Magnetic and Thermal Studies of Co(II), Ni(II), Cu(II) and Pd(II) Chelates of 4-S-Benzyl-1-*p*-Cl-Phenyl-5-Phenyl-2, 4-Isodithiobiuret (BPPTB)

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Manuscript received 3 January 1980, revised 27 May 1980, accepted 9 July 1980

Studies on the chelates of Co(II), Ni(II), Cu(II) and Pd(II) metal ions with the bidentate ligand 4-S-benzyl-1-p-Cl-phenyl-5-phenyl-2, 4-isodithiobiuret have been carried out. On the basis of the elemental analysis, thermal analysis and molar conductivity data, the chelates have been assigned as $Co(BPPTB)_2$, $Ni(BPPTB)_2$, $Cu(BPPTB)_2.2H_2O$ and $Pd(BPPTB)_2$. Their electronic spectra, magnetic susceptibility as well as infrared spectra have been reported and discussed. Ni(II) chelate exhibits anomalous magnetic moment (μ = 1.06B.M.) at room temperature. This nature of Ni(II) chelate is discussed on the basis of the work reported earlier.

A literature survey showed that not much work has been done on the complex formation of dithiobiuretes[1-4]. The complexes of 1, 5-disubstituted-2, 4-dithiobiuret with Cu(II), Ni(II), Co(II) and Zn(II) were studied by Srivastava and Agarwal[5,6]. Recently, Pignedoli *et al*[7] have prepared the neutral and cationic complexes of Ni(II) with 1-phenyl-5-methyl-2, 4-dithiobiuret and suggested a tentative structure on the basis of electronic and infrared spectra. Kowel *et al*[8] have explained the structure of the inner coordination sphere and bonding in Cu(II) and Ni(II) complexes of 2, 4-dithiobiuret using infrared and Raman spectra. In this communication, we report the preparation and properties of complexes of Co(II), Ni(II), Cu(II) and Pd(II) with ligand. Tentative structure have been proposed for the chelates on the basis of spectral and magnetic susceptibility data and the results of chemical and thermal analysis and molar conductivity data.

Experimental

The chemicals used were all of AnalaR or chemically pure grade.

Preparation of the ligand :

4-S-benzyl-1-parachloro-phenyl-5-phenyl-2, 4-isodithiobiuret (BPPTB) was reported in literature in 1903 by Johnson and Elmer[9]. However, in the present studies it has been synthesised by simple method as modified by Mahajan *et al*[10].

Preparation of the Metal Chelates :

Metal salts of Co(II), Ni(II) and Cu(II) were used in the form of their acetates in the preparation of their chelates, while Pd(II) was taken in the form of chloride. All the solutions of metal salts except Pd(II) were prepared in distilled water while the solution of Pd(II) chloride was prepared in dilute HCl adjusting its *p*H between 0.5-1.0. Ligand solution was prepared in methanol.

An aqueous solution of metal salts was gradually added with vigorous stirring to the methanolic solution of reagent in 1 : 2 (M : L) molar ratio. The solution was diluted with distilled water till coloured chelates separated out. It was digested on water bath for about 15 minutes, cooled, filtered and washed with hot water and methanol several times. It was dried in an desiccator over calcium chloride and recrystallised from solvent ether. The results of analysis of the chelates are given in Table 1.

Physical Measurements :

Magnetic measurements (Tables 1 and 2), visible and ultra violet spectra (Tables 3 and 4), reflectance spectra (Table 3), infrared spectra (Table 5) and conductance measurements for all the chelates were studied as reported earlier[11]. T.G.A. studies were performed in the Chemistry Department of I.I.T., Bombay[12]. The thermoanalytical data of the chelates in the present study is detailed in Table 6.

Results and Discussion

Magnetic Measurements :

The magnetic moment of Co(II) chelate of BPPTB is 4.65 B.M. at room temperature. Carlin[13] observed a magnetic moment value of 4.73 B.M. for Co(II) complex of ethylene thiourea at room temperature and it is temperature independent, with the value of $\Theta = -11°K$ and suggested tetrahedral geometry to the Co(II) complex. In the present case magnetic moment value are

TABLE 1—ANALYTICAL DATA, COLOUR, MOLAR CONDUCTANCE IN NITROBENZENE AND μ_{eff} AT ROOM TEMPERATURE

Chelate	M% Found (Reqd)	C% Found (Reqd)	H% Found (Reqd)	N% Found (Reqd)	S% Found (Reqd)	Colour	M*	μ_{eff} B.M. (294.5°K)
$Co(BPPTB)_2$	6.72 (6.69)	58.20 (57.27)	4.04 (3.86)	9.50 (9.54)	14.50 (14.54)	Green	5.00	4.65
$Ni(BPPTB)_2$	6.75 (6.67)	57.80 (57.29)	3.89 (3.86)	9.30 (9.54)	14.20 (14.55)	Blue	3.90	1.06
$Cu(BPPTB)_2.2H_2O$	6.85 (6.90)	52.10 (54.74)	3.97 (4.12)	9.12 (9.20)	13.65 (13.90)	Light green	10.95	1.99
$Pd(BPPTB)_2$	11.35 (11.47)	54.00 (54.34)	3.70 (3.66)	9.15 (9.05)	13.90 (13.84)	Orange	9.50	Dia

M* = Molar Conductance M(ohm^{-1}.cm^2.mol^{-1}) in $1 \times 10^{-3} M$ solution of nitrobenzene at 25°.

TABLE 2—MAGNETIC DATA AT DIFFERENT TEMPERATURES

Temperature (°K)	Co(II)-BPPTB Diamagnetic correction: -189×10^{-6} erg G^{-2}mole^{-1}			Temperature (°K)	Cu(II)-BPPTB Diamagnetic correction: -215×10^{-6} erg G^{-2} mole^{-1}		
	χ Co $\times 10^6$ (erg G^{-2} mole^{-1})	χ Co$^{-1} \times 10^{-3}$ (G^2 mole erg^{-1})	μ_{eff} (B.M.)		χ Cu $\times 10^6$ (erg G^{-2}mole^{-1})	χ Cu$^{-1} \times 10^{-3}$ (G^2 mole erg^{-1})	μ_{eff} (B.M.)
294.5	9,205	1.086	4.65	294.5	1,6949	5.900	1.99
278.0	9,890	1.011	4.65	260.5	1,8869	5.300	1.98
250.0	10,820	0.925	4.65	245.0	1,9973	5.006	1.97
210.5	12,882	0.776	4.66	210.0	2,2769	4.392	1.95
178.0	15,607	0.640	4.65	150.0	3,2269	3.098	1.96
104.0	25,970	0.389	4.65	102.0	4,5726	2.198	1.93
	$\Theta = -9$°K				$\Theta - 10$°K		

TABLE 3—ELECTRONIC SPECTRAL BANDS AND THEIR ASSIGNMENTS

Complex	Reflectance spectra λ_{max} nm	kK	Absorption spectra (Chloroform) λ_{max} nm	kK	Assignment
Co(II)-BPPTP	690	14.50	700(sb)	14.28	
	630	15.87	600	16.66	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
	520	19.23	520	19.23	
Ni(II)-BPPTB	670	14.92	620	16.12	$^1A_{1g} \rightarrow {}^1B_{1g}$
	640	15.62			
	580	17.41	560	17.85	$^1A_{1g} \rightarrow {}^1B_{2g}$
Cu(II)-BPPTB	870	11.49			$^2B_{1g} \rightarrow {}^2A_{1g}$
	700	14.29	720	13.88	$^2B_{1g} \rightarrow {}^2B_{2g}$
	620	16.23	640	15.62	
			550	18.18	$^2B_{1g} \rightarrow {}^2E_g$
Pd(II)-BPPTB			510	19.61	$^1A_{1g} \rightarrow {}^1B_{1g}$
	410	24.30			
			350	38.57	$^1A_{1g} \rightarrow {}^1E_{1g}$
			280	35.71	$^1A_{1g} \rightarrow {}^1E_u$

TABLE 4—ABSORPTION SPECTRA OF THE LIGAND AND ITS METAL CHELATE IN UV REGION

Species	λ_{max} nm	λ_{max} nm	log ϵ	Assignments
BPPTB	310	32.26	3.85	$\pi \rightarrow \pi$
$Co(BPPTB)_2$	300	33.33	4.63	$\pi \rightarrow \pi^*_4$
	245	40.82	4.52	$Py\pi \rightarrow \pi$, $\pi \rightarrow d$
$Ni(BPPTB)_2$	295	33.90	4.62	$\pi_3 \rightarrow \pi^*_4$
	245	40.82	4.51	$Py\pi \rightarrow \pi$, $\pi \rightarrow d$
Cu(BPPTB)	270	37.04	4.53	$\pi_3 \rightarrow \pi^*_4$
	245	40.82	4.60	$Py\pi \rightarrow \pi$, $\pi \rightarrow d$

temperature independent, (Table 2 and $\Theta = -9$ K.) This indicates tetrahedral character of Co(II) chelate of BPPTB. The magnetic moment of Ni(II) chelate is found to be 1.06 B.M. which is unusual and lower than spin only value of two unpaired electrons. Holt *et al*[14] and others[15-17] suggested that partial paramagnetic moment of Ni(II) complex may be attributed to the square planar tetrahedral equilibrium. Therefore, a square planar geometry can be suggested for Ni(II) chelate in the present case. Magnetic moment value of Cu(II) chelate is nearly same over a temperature range 100-294.5°K which obey the Curie-Weiss law and have a $\Theta = 10$°K indicating neither inter nor intramolecular Cu–Cu interaction[18]. Chelate of Pd(II) in the present study is diamagnetic, hence square planar geometry is suggested.

Electronic Spectra :

The diffuse reflectance spectra and absorption spectra in chloroform of Co(II)-BPPTB chelate exhibit intense multiple bands in the region 14 kK-19.25 kK. On the basis of experimental results and observation made by earlier workers[19,20], a tetrahedral geometry can be suggested for Co(II)-BPPTB chelate and multiple bands in the electronic spectra at 14 kK-19.25 kK can be accounted for $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions. The reflectance and absorption spectra of Ni(II)-BPPTB chelate show multiple bands

TABLE 5—INFRARED AND SPECTRAL DATA OF BPPTB AND METAL COMPLEXES

BPPTB	Co(II)	Ni(II)	Cu(II)	Pd(II)	Assignments
$3560_{m,sp}$	—	—	—	—	N – H-ph stretching
3200_{sp}	3260_{sp}	3380_{sp}	3200_{b}	3100_{b}	N – H stretching
1560_{sp}	1590_{sp}	1590_{sp}	$1590_{b,m}$	$1600_{m,sp}$	C – N stretching
1400_{b}	1390_{sp}	1390_{sp}	1400_{sp}	$1400_{m,sp}$	S – CH_2 stretching
1210_{sp}	1200_{sp}	1200_{sp}	1200_{sp}	$1215_{m,sp}$	S – CH_2 – ph
695_{sp}	690_{sp}	690_{sp}	690_{sp}	690_{sp}	C = S stretching
—	—	—	3400_{b}	—	Lattice water
—	540_{m}	$520_{m,w}$	$530_{m,w}$	530_{w}	M – N
—	$390\text{-}420_{w}$	$380\text{-}400_{m}$	$410\text{-}420_{w}$	$390\text{-}420_{m,w}$	M – S

m = medium , sp = sharp , w = weak ; b = broad.

TABLE 6—THERMOANALYTICAL DATA OF METAL COMPLEXES OF BPPTB

Temperature °C	%weight loss Found	Calculated	Probable composition
	$Co(BPPTB)_2$		
560	87.00	90.88	Co_3O_4
	$Ni(BPPTB)_2$		
580	89.00	91.51	NiO
	$Cu(BPPTB)_2.2H_2O$		
190	4 50	3.90	$Cu(BPPTB)_2$
540	89.00	91.36	CuO
	$Pd(BPPTB)_2$		
640	87.50	86.81	PdO

around 15 kK-18 kK. The bands at 14.92 kK and 17.41 kK may be assigned to $^1A_{1g} \rightarrow {^1B_{1g}}$ and $^1A_{1g} \rightarrow {^1B_{2g}}$ transitions respectively[21]. Drago[22] and Holm[23] have suggested tetragonal or square planar geometry for Ni(II) complexes on the basis of similar spectral transition. The diffuse reflectance spectra of Cu(II)-BPPTB chelate show a band in 11 kK-20 kK region and absorption spectra show bands with shoulder in the range 12 kK-24 kK. Hatway *et al*[24,25] have also observed two main bands at about 14 kK-15.60 kK and 9.20 kK-10.80 kK in the electronic spectra of Cu(II) complexes and suggested distorted octahedral geometry for Cu(II) complexes. The observed electronic spectra of Pd(II) chelate suggest square planar geometry for this chelate[26,27].

Electronic spectra in the UV region of the metal chelates and ligand show two or more bands in range of 32-37 kK (Table 4). Transitions of the band and their assignments are given in Table 4. The trends of the bands are in good agreement with the observations made by earlier workers[28-31].

Infrared Spectra :

On examination of ir spectra of ligand (BPPTB) a strong band has been observed at 3050-3150 cm^{-1}. This band is due to –NH stretching vibration[32,33,34]. The weakening of the –NH stretching frequency is observed on the chelate formation with a shift to slight higher frequency, which may probably be caused by the drainage of the electrons from the nitrogen to metal atom upon chelation[35]. The ir spectra of ligand show one sharp band at 1400 cm^{-1} and strong band at 1210 cm^{-1} which may be assigned to the $-S-CH_2$ and $-C-S-CH_2$-ph respectively[34]. These have been found at same position in the metal chelates with medium or nearly same intensity. This observation may suggest that $-S-CH_2$-ph is free in the chelate and indicative of not taking part in the chelate formation. Another strong band at 1550 cm^{-1} [34] in ligand may be assigned to C – N stretching frequency, which appears at 1580-1600 cm^{-1} in the metal chelates. A fairly strong band at 1500 cm^{-1} in the ligand and metal chelates may be due to mixed vibration of C = S stretching, – C – N stretching and – NH bonding modes[36,37]. A fairly sharp band at 720-690 cm^{-1} in the ligand has been found at nearly the same position in metal chelates. This indicates major contribution of C = S stretching and C – N bonding vibration[36,38]. An increase of the C N stretching frequency and a decrease of the same C – S frequencies for the metal chelates with respect to ligand indicate that ligand is coordinated to the metal through S atom[31,39]. In the region 500-550 cm^{-1}, the metal chelates show a new absorption peak which is not observed in the spectra of ligand. Various workers[40-44] have assigned the M – N stretching modes in the Co, Ni, Cu and Pd chelates to the bands in the region 500-600 cm^{-1}. Metal-sulphur stretching frequencies usually lie within the range 480-210 cm^{-1} [31,40,45-47].

Thermogravimetric Analysis :

Chelates of Co(II) and Ni(II) : The mass loss curves of these chelates are shown as curve A and B in Fig. 1. Examination of TG curve indicates that both the chelates do not contain water of hydration. Co(II) chelate is stable upto 110° and after the decomposition takes place as shown by rapid mass loss curve. Ni(II) chelate is found to be stable upto 200° and further rapid mass loss is observed due to oxidation reduction reactions.

Chelate of Cu(II) : According to the mass loss curve (Fig. 1, Curve C) $Cu(BPPTB)_2.2H_2O$ loses its water of hydration in one step between 100° and 190° (4.50% found, 3.90% ther.) followed by rapid mass loss.

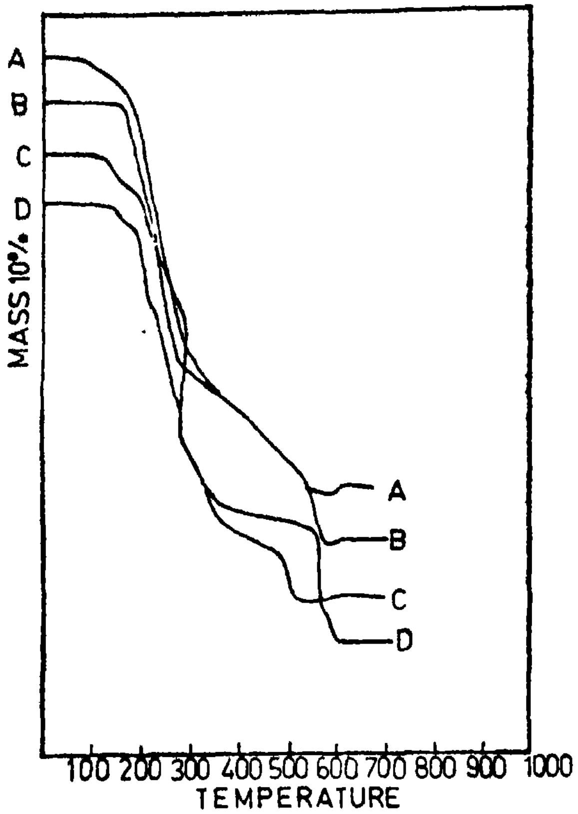


Fig. 1. TGA Curves

Chelate of Pd(II) : This chelate contain no water of hydration (Fig. 1, Curve D) and is found to be stable upto 150°, after that continuous mass loss is observed.

In all the chelates of BPPTB except $Pd(BPPTB)_2$ chelate it is observed that there is small increase in the weight of residue after 500° [for $Co(BPPTB)_2$ – weight of the residue increases beyond 595°, for $Ni(BPPTB)_2$ – weight of the residue increases beyond 600° while for $Cu(BPPTB)_2.2H_2O$ – weight of the residue increases beyond 540]. Such type of results have been obtained by Sceney *et al*[4,8,46] and suggested that the increase in weight is due to the oxidation of Cu_2S to CuO and $CuSO_4$.

Acknowledgement

Authors are thankful to Prof. K. N. Munshi, Head, Department of Chemistry, Nagpur University, for providing the facilities.

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J. Indian Chem. Soc.
Vol. LVII, September 1980, pp. 876-883

The Spectrophotometric and Ion-Selective Electrode Determinations of $MgSO_4$ Association at High Ionic Strengths

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Manuscript received 4 January 1979, revised 19 February 1980, accepted 4 July 1980

The stoichiometric stability constants for $MgSO_4$ association in aqueous solution have been determined spectrophotometrically and potentiometrically in the ionic strength range of 0.3 to 1.0*M*, and 0.10 to 0.82*M*, respectively. Terpyridine is used as a metal ion indicator to monitor the free magnesium ion concentrations and divalent cation-selective electrode is employed to measure the free magnesium ion activities in pure $MgSO_4$ solutions. The results obtained at 25° by the two methods show that they are in good agreement.

MOST of the $MgSO_4$ stability constants were determined at low concentrations and extrapolated to zero ionic strength by making use of the Debye-Hückel theory. We now wish to report the concentration quotient stability constants determined at ionic strength varying from 0.10 to 1*M*. First of all, the $MgSO_4$ association reaction is the major 1 : 1 divalent ionic reaction in seawater which has an ionic strength around 0.7 *M*[1]. Secondly, the use of ionic-selective electrodes to study thermodynamics of ion pair formation processes is still at its infancy and some controversial questions about this technique have been raised by some investigators[2].

Here the $MgSO_4$ association was studied by the ion-selective electrodes as well as the spectrophotometric method. The agreement between their results serves the purpose of confirming to some degree the reliability of both techniques. The spectrophotometric method of using a metal ion indicator to determine the $MgSO_4$ association possesses several interesting features. It can be extended to other systems such as the reactions under high pressures (i.e., the ionic reactions beneath the surface of the sea) where the ion-selective electrode method fails, or the ion-molecule reactions where the conductance measurements can no longer be applied.

For the purpose of determining the association constant at various ionic strengths, different concentrations were prepared by dilution of the stock solutions immediately before running the experiments. Normally we used 200 ml solution for each measurement and constant stirring was taking place while doing the experiment. The potential reading of the solution was recorded with time until a constant mv reading is reached. This usually takes 6-10 minutes. This period of time was also necessary but sufficient to bring about the temperature of the solution in the cell to equilibrium at 25°. The calibration curve was done side by side as the experiment was in progress. In other words, a measurement of standard reference $MgCl_2$, and test solution, $MgSO_4$ immediately following each other. These two solutions were made to have as close value of mv as possible to assure close values of activity for the free Mg^{+2} ion. The experimental Nernst slope for the calibration curve was always ~29.6 mv in good agreement with the theoretical value at 25°. The *p*H values of the measured solutions were determined right before running the experiment. It was found around 8. Therefore, no adjustment was needed since, according to the Orion Manual, this is the right *p*H values for the present potential measurements. For each individual concentration, the measurement was repeated four or five times. Each time freshly prepared solution was used. This was necessary for establishing a good mean value for the $MgSO_4$ association constant at a certain ionic strength. The variation of ionic strength was accomplished by varying the $MgSO_4$ concentration. To fix the ionic strength by adding some inert electrolyte was avoided due to the complications which might have arisen such as the potentiometric response to the inert cation and its electrostatic interactions with $SO_4^=$ ions. In the present study, the pure $MgSO_4$ electrolyte was used to prepare the solution. Therefore the activity of Mg^{+2} ion in $MgSO_4$ solution can be measured using $MgCl_2$ as a standard reference in conjunction with the Nernst equation. To convert the activities to concentrations, activity coefficients (γ) are needed. Various sets of γ values have appeared in the literature. In our calculation, the γ values listed in the Orion Manual[6] were used. Practically, it does not make too much difference which values of activity coefficients are used, as long as the same set of values has been used to obtain both the calibration

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curve and the Mg^{+2} ion concentration in $MgSO_4$ solutions. The relative errors in activity coefficients are thus greatly minimized.

Experimental

A. The Spectrophotometric Method :

Materials and Preparations :

Reagent grade $MgCl_2$ (Merck), $MgSO_4$ (Fisher Scientific) were used and the concentrations were standardized by EDTA titrations. Tetramethylammonium chloride (TMA) purchased from Eastman was recrystallized from a hot methanol-acetone mixture[6]. Terpyridine obtained from Pfaltz and Bauer was standardized spectrophotometrically at 290 nm ($\epsilon = 1.6 \times 10^4$).[4] Stock solutions were prepared for the above reagents and were subsequently diluted to desired concentrations with deionized distilled water.

Measurements :

The pH of the solution adjusted around 8 right before the absorbance measurement was made on a Zeiss spectrophotometer equipped with 1 cm cells. The spectrophotometric measurements were made at 329 nm near one of the peaks for the magnesium-terpyridine complex and at 290 nm near the peak for the free terpyridine base, respectively. The electronic absorption spectra for the complex and free terpyridine are shown in Figure 1.

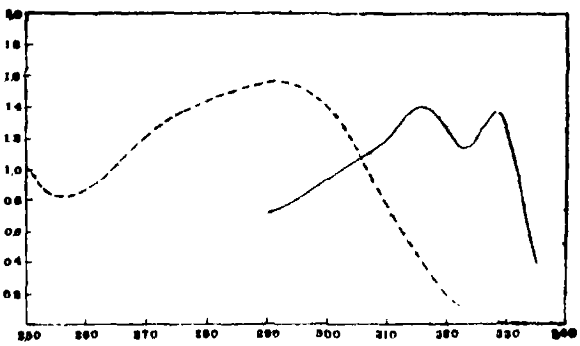


Fig. 1. Electronic Absorption Spectra for the Free Terpyridine Base and Its Mono-Magnesium Complex at 25°C.
············ $0.98 \times 10^{-4} M$ Terpyridine
———— $0.98 \times 10^{-4} M$ Terpyridine and $0.3 M$ $MgCl_2$.

B. The Ion-Selective Electrode Method :

Preparations and Measurements :

The potential measurements were made with an Orion model 92-32 divalent cation electrode, an Orion model 90-01 single junction reference electrode, and an Orion model 801 pH-mv meter.

The temperature of the solutions was maintained at 25±0.1° in a constant temperature bath. The cell was described elsewhere[6]. All solutions were prepared as described previously.

Results and Discussion

A. The Spectrophotometric Method :

The selection of terpyridine as a metal ion indicator to study $MgSO_4$ association was based on the following considerations. (A) It possesses high extinction coefficients both as a free ligand and a coordinated one at two well separated wavelengths. (B) It has sufficient solubility and remains stable in aqueous solution. (C) It acts as a neutral ligand at pH higher than 7, therefore its reaction with Mg^{+2} ions is expected to be ionic strength insensitive. (D) As a weak base ($pK_1 = 4.7, pK_2 = 3.3$), it eliminates the complications caused by the participation of protonated ligand in the reaction.

Magnesium-Terpyridine Interactions :

The stability constant, K_I, for the formation of 1 : 1 magnesium-terpyridine complex, MgI^{+2}, from the free ligand, I, and the free magnesium ion may be expressed as

$$Mg^{+2} + I \rightleftharpoons MgI^{+2} \quad \text{(A-1)}$$

In all experiments described in this paper the concentration of magnesium was at least 500 fold higher than that of the ligand, so that the known total magnesium concentration can be assumed for the free magnesium ion concentration. Then we have

$$A = \epsilon_{MgI}[MgI^{+2}] + \epsilon_I[I] \quad \text{(A-2)}$$

$$\Sigma I = [MgI^{+2}] + [I] \quad \text{(A-3)}$$

$$K_I = \frac{[MgI^{+2}]}{[Mg^{+2}][I]} \quad \text{(A-4)}$$

where ϵ_{MgI} and ϵ_I are the extinction coefficients for the metal complex and the free ligand at a certain wavelength, respectively. A is the absorbance measured at that wavelength. ΣI represents the known total ligand concentration. Both A and ϵ_I can be determined experimentally.

Two of the four unknowns (ϵ_{MgI}, K_I, $[MgI^{+2}]$ and [I]) in the above three equations A-2 through A-4 may be eliminated to obtain a simplified equation with two remaining unknowns,

$$\frac{\Sigma I \times [Mg^{+2}]}{A - \epsilon_I \times \Sigma I} = \frac{1}{K_I(\epsilon_{MgI} - \epsilon_I)} + \frac{[Mg^{+2}]}{(\epsilon_{MgI} - \epsilon_I)} \quad \text{(A-5)}$$

A plot of equation A-5 gives slope and intercept which lead to the values for ϵ_{MgI} and K_I respectively.

TABLE A-1 — THE ABSORBANCE MEASUREMENTS AND CALCULATED VALUES FOR 1 : 1 MAGNESIUM TERPYRIDINE COMPLEX AT 25°C

Sl. No.	$MgCl_2$ (*M*)	Terpy (*M* × 10^4)	$N(CH_3)_4Cl$ (*M*)[a]	$A_{(329\ nm)}$	$A_{(290\ nm)}$	$\frac{\Sigma I[Mg^{+2}]}{[A - \epsilon_I \Sigma I]_{329\ nm}} \times 10^{5b}$	$\frac{\Sigma I[Mg^{+2}]}{[A - \epsilon_I \Sigma I]_{290\ nm}} \times 10^{5b}$
1.	1.00	1.0		1.762	0.420	5.737	−8.475
2.	0.50	1.0		1.568	0.562	3.226	−4.817
3.	0.40	1.0		1.458	0.627	2.788	−4.111
4.	0.30	1.0		1.333	0.725	2.281	−3.429
5.	0.30	0.5		0.683	0.362	2.226	−3.425
6.	0.25	1.0		1.214	0.775	2.091	−3.080
7.	0.20	1.0		1.105	0.865	1.840	−2.719
8.	0.20	0.5		0.565	0.432	1.799	−2.717
9.	0.15	1.0		0.949	0.968	1.612	−2.378
10.	0.10	2.0		1.548	2.115	1.323	−1.843
11.	0.10	1.0		0.759	1.093	1.350	−1.972
12.	0.20	1.0	0.3	1.067	0.865	1.925	−2.721
13.	0.10	1.0	0.3	0.748	1.104	1.389	−2.016
14.	0.20	1.0	0.3	1.114	0.840	1.842	−2.740
15.	0.15	1.0	0.3	0.968	0.979	1.596	−2.415
16.	0.25	1.0	0.3	1.235	0.781	2.071	−3.064
17.	0.30	1.0	0.3	1.304	0.715	2.351	−3.390
18.	0.40	1.0	0.3	1.498	0.628	2.721	−4.115
19.	0.50	1.0	0.3	1.557	0.556	3.270	−4.789
20.	1.00	1.0	0.3	1.762	0.422	5.767	−8.489

[a] TMA (1.5*M*) has an absorbance of 0.016 at 329 nm and 0.038 at 290 nm, respectively

[b] ϵ_I is 188 M^{-1} cm^{-1} at 329 nm in the absence of TMA, it is 280 at 329 nm and 1.6×10^4 M^{-1} cm^{-1} at 290 nm in the presence of TMA.

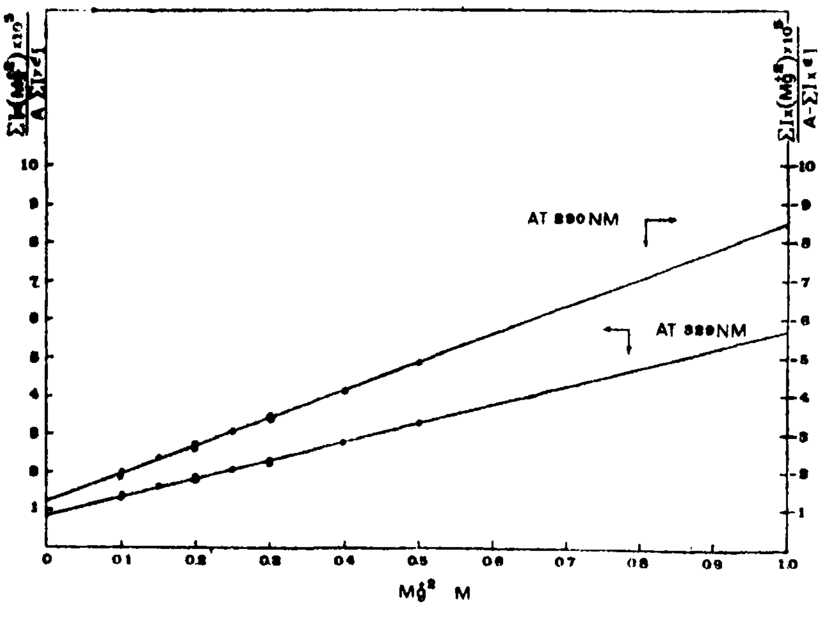


Fig. 2. Plots of Equation A-5 based on the points shown in Table A-1 in the absence of TMA at 25°C.

The experimental results are collected in Table A-1. The plots based on equation A-5 and the data in Table A-1 are shown in Figure 2. The values for K_I and ϵ_{MgI} determined at 329 nm are 5.835 M^{-1} and 2.070×10^4 M^{-1} cm^{-1} ; and at 290 nm ; they are 5.881 M^{-1} and $2.191 \times 10^3 M^{-1}$ cm^{-1}, respectively. As shown, the K_I values obtained independently with the exclusion of the points having TMA added at these two wavelengths are in excellent agreement with an average value of $5.858 \pm 0.023 M^{-1}$.

By utilizing equation A-2 twice and the independently determined ϵ_{MgI} and ϵ_I values at 329 and 290 nm, respectively, the concentrations for $[MgI^{+2}]$ and [I] along with K_I may be regenerated. As compared to the known total ligand concentration, the calculated sum, $[MgI^{+2}]+[I]$ has less than

1% error, and the regenerated mean K_I value deviates from 5.855 M^{-1} only by ±3.3%. These errors represent the minimum errors as the points of measurements increased up to $MgCl_2 = 1.0\ M$ as shown in Table A-1. An additional point at $MgCl_2 = 1.5\ M$ was also spectrophotometrically determined. With the inclusion of this point, the errors for the regenerated K_I value jumped to more than twice as much. Therefore the point at $MgCl_2 = 1.5\ M$ which has an ionic strength of 4.5 M was disregarded.

To investigate the ionic strength effect on the stability constant K_I, TMA was added to the magnesium-terpyridine system. The results are combined in Table A-1. An analysis of this table shows that the absorbance changes for the magnesium-terpyridine system due to the presence of TMA are within experimental error in Table A-1. With the inclusion of these points, the plots based on eq A-5 and all the data at both 329 nm and 290 nm give an average value of 5.684±0.001 for K_I. The values for ϵ_{MgI} are 2.079×10^4 at 329 nm and $2.06 \times 10^8\ M^{-1}\ cm^{-1}$ at 290 nm respectively. The 3.4% decrease in slope as compared to the previous one of 5.858 M^{-1} may be brought about by a very weak polar interaction between TMA and terpyridine as indicated by the fact that extinction coefficients for terpyridine increases slightly at 329 nm in the presence of TMA, and it remains constant at 290 nm despite that TMA absorbs weakly at this wavelength, (see foot-notes in Table A-1). As a result of this observation the $[TMA]/[Mg^{+2}]$ ratios in Table A-1 were kept below 3 to minimize the errors brought by the introduction of TMA to the solutions.

Magnesium Sulfate Interactions :

On the basis of conductance measurements, $MgCl_2$ undergoes complete dissociation to give Mg^{+2} and Cl^- ions in aqueous solution. Therefore eq. A-1 represents the only possible reaction between $MgCl_2$ and terpyridine. In the case of $MgSO_4$, the reaction is complicated by the formation of outer and inner sphere mixed complexes, namely,

$$\begin{array}{ccccc} Mg^{+2}(aq)+SO_4^{-2}(aq) & \rightleftharpoons & Mg^{+2}(aq)SO_4^{-2} & \rightleftharpoons & MgSO_4(aq) \\ + & & + & & + \\ I & & I & & I \\ \updownarrow & & \updownarrow & & \updownarrow \\ MgI^{+2}(aq)+SO_4^{-2}(aq) & \rightleftharpoons & MgI^{+2}(aq)SO_4^{-2} & \rightleftharpoons & MgISO_4(aq) \end{array} \quad \text{(A-6)}$$

In this reaction, the association constant K_{MgSO_4}, is designated as

$$K_{MgSO_4} = \frac{[MgSO_4]_T}{[Mg^{+2}][SO_4^{-2}]} = \frac{[Mg]_T - [Mg^{+2}]}{[Mg^{+2}][SO_4^{-2}]} \quad \text{(A-7)}$$

where $[MgSO_4]_T$ is defined as the sum of inner and outer sphere ion pairs.

Since the measured absorbance in the mixture of $MgCl_2$-$MgSO_4$-Terpyridine reflects all types of magnesium terpyridine complexes, the Beer's law for eq. A-6 becomes

$$A = \epsilon_{MgI}[MgI^{+2}] + \epsilon_Y[Y] + \epsilon_Z[Z] + \epsilon_I[I] \quad \ldots \quad \text{(A-8)}$$

where [Y] and [Z] represent $[MgI^{+2}(aq)SO_4^{-2}]$ and $[MgISO_4(aq)]$ respectively. ϵ_Y and ϵ_Z are their respective extinction coefficients.

With new terms defined as

$$K_Y = [Y]/[MgI^{+2}][SO_4^{-2}] \text{ and}$$
$$K_Z = [Z]/[MgI^{+2}][SO_4^{-2}],$$

eq. A-8 can be rearranged as

$$A = \epsilon_{MgI}[MgI^{+2}]\left\{1 + \frac{\epsilon_Y K_Y + \epsilon_Z K_Z}{\epsilon_{MgI}}[SO_4^{-2}]\right\} + \epsilon_I[I]$$
$$= \epsilon_{MgI}\{[MgI^{+2}]\beta\} + \epsilon_I[I] \quad \ldots \quad \text{(A-9)}$$

If the calculated $[MgI^{+2}]\beta$ was assumed for $[MgI^{+2}]$, the free Mg^{+2} ion concentration calculated from eq. A-4 would be a factor of β higher than the true value. At a constant ionic strength, β is a function of $SO_4^=$ concentration as shown in eq. A-9. The solutions with varying $SO_4^=$ concentrations at a constant ionic strength were made possible by adding $MgCl_2$ to the test solutions. The evaluation of $[MgI^{+2}]\beta$ and [I] from eq. A-9 will be described later. In the present study, we found that the association constant, K_{MgSO_4}, evaluated at constant ionic strength is independent of $SO_4^=$ ion concentrations (see Table A-2). This implies that the use of terpyridine as a metal ion indicator in the $MgSO_4$ solution forms only 1 : 1 magnesium-terpyridine complex free of SO_4^{-2} interactions. This is because that Mg^{+2} ion in the Mg-Terpy^{+2} form sterically hinders its interaction with $SO_4^=$. Then it is justified to exclude the two species, Y and Z from equation A-6. A similar case is found in magnesium *m*-benzene-disulfonate where the benzene ring blocks the formation of inner and outer sphere ion pairs in aqueous solution despite the electrostatic attractions between the ions. However, this is not the case for bipyridine used as an indicator for the $MgSO_4$ system where K_{MgSO_4} was found slightly dependent on $SO_4^=$ concentrations at constant ionic strength. A plausible explanation is that terpyridine has a larger molecular size than bipyridine.

Since the concentrations for $[MgI^{+2}]$ and [I] are not related to the wavelength chosen for the absorbance measurements, equation A-2 can be used twice at 329 and 290 nm to solve the concentrations simultaneously to eliminate the error in $[MgI^{+2}]$ reflected in [I] or vice versa. Then the Mg^{+2} ion concentrations can be obtained based on calculated $[MgI^{+2}]$, [I] and previously determined K_I values. The extinction coefficients and K_I value obtained

Table A-2—Experimental Results for the $MgSO_4$ Association Constant Determinations Using Terpyridine as a Metal Ion Indicator at 25°C. I_s Represents Ionic Strength

Sl. No.	$MgCl_2$ (M)	$MgSO_4$ (M)	$N(CH_3)_4Cl$ (M)	Terpy ($M \times 10^4$)	$A_{(329 nm)}$	$A_{(290 nm)}$	MgI^a ($M \times 10^4$)	I^a ($M \times 10^4$)	[MgI+I] ($M \times 10^4$)	Mg^{+2} (M)	SO_4^{-2} (M)	K	I_s
1.		0.60		1.0	1.232	0.776	0.5916	0.4040	0.9956	0.2500	0.2500	5.6	1.00
2.		0.55		1.0	1.207	0.805	0.5793	0.4238	1.0031	0.2333	0.2333	5.8	0.93
3.		0.50		1.0	1.153	0.835	0.5531	0.4462	0.9993	0.2116	0.2116	6.4	0.85
4.		0.45		1.0	1.115	0.865	0.5345	0.4675	1.0020	0.1952	0.1952	6.7	0.78
5.		0.40		1.0	1.054	0.911	0.5048	0.5003	1.0051	0.1722	0.1722	7.7	0.69
6.		0.35		1.0	1.007	0.961	0.4817	0.5347	1.0164	0.1538	0.1538	8.3	0.62
7.		0.35		1.5	1.473	1.433	0.7046	0.7992	1.5037	0.1505	0.1505	8.8	0.60
8.		0.30		1.0	0.915	0.986	0.4374	0.5564	0.9938	0.1342	0.1342	9.2	0.54
9.		0.25		1.0	0.844	1.045	0.4021	0.5980	1.0004	0.1149	0.1149	10.2	0.46
10.		0.20		1.0	0.757	1.108	0.3600	0.6342	1.0032	0.0955	0.0955	11.5	0.38
11.	0.20	0.20		1.0	1.280	0.740	0.6150	0.3783	0.9933	0.2775	0.0775	5.7	0.91
12.	0.22	0.18		1.0	1.299	0.727	0.6243	0.3689	0.9932	0.2889	0.0689	5.6	0.94
13.	0.25	0.15		1.0	1.348	0.713	0.6456	0.3573	1.0029	0.3084	0.0584	5.1	0.98
14.	0.20	0.15		1.0	1.264	0.773	0.6071	0.4000	1.0071	0.2591	0.0591	5.9	0.84
15.	0.15	0.20		1.0	1.196	0.811	0.5740	0.4283	1.0023	0.2288	0.0788	6.7	0.77
16.	0.15	0.15		1.0	1.146	0.841	0.5496	0.4504	1.0000	0.2088	0.0588	7.6	0.68
17.	0.15	0.15		1.5	1.671	1.268	0.8012	0.6828	1.4840	0.2003	0.0503	9.9	0.65
18.	0.18	0.12		1.0	1.187	0.817	0.5696	0.4327	1.0023	0.2247	0.0447	7.5	0.72
19.	0.13	0.20		1.0	1.150	0.825	0.5517	0.4401	0.9918	0.2140	0.0840	6.5	0.73
20.	0.08	0.09		1.0	0.847	1.038	0.4039	0.5935	0.9974	0.1162	0.0362	12.8	0.38
21.	0.10	0.06		1.0	0.875	1.009	0.4176	0.5735	0.9911	0.1243	0.0243	11.8	0.40
22.	0.12	0.08		1.0	0.973	0.947	0.4654	0.5282	0.9936	0.1504	0.0304	10.8	0.48
23.	0.12	0.06		1.0	0.932	0.956	0.4455	0.5365	0.9820	0.1418	0.0218	12.4	0.45
24.	0.12	0.121		1.0	1.026	0.902	0.4913	0.4965	0.9878	0.1689	0.0489	8.7	0.56
25.		0.30	0.20	1.0	0.978	0.968	0.4619	0.5486	1.0105	0.1481	0.1481	6.9	0.79
26.		0.20	0.40	1.0	0.825	1.067	0.3900	0.6166	1.0066	0.1113	0.1113	7.2	0.85
27.	0.15	0.10	0.20	1.0	1.086	0.862	0.5171	0.4721	0.9892	0.1927	0.0427	7.0	0.82
28.		0.30	0.10	1.0	0.942	0.978	0.4470	0.5505	0.9975	0.1429	0.1429	7.7	0.67
29.	0.10	0.10	0.12	1.0	0.946	0.960	0.4490	0.5421	0.9911	0.1457	0.0457	8.2	0.60
30.	0.08	0.09	0.11	1.0	0.894	1.037	0.4234	0.5935	1.0169	0.1255	0.0455	7.8	0.53
31.		0.20	0.21	1.0	0.800	1.077	0.3779	0.6244	1.0023	0.1065	0.1065	8.2	0.64
32.		0.20	0.30	1.5	1.163	1.608	0.5514	0.9339	1.4853	0.1039	0.1039	8.9	0.62
33.	0.10	0.10	0.20	1.0	0.964	0.981	0.4575	0.5542	1.0117	0.1452	0.0452	8.8	0.68
34.	0.10	0.08	0.24	1.0	0.924	0.989	0.4382	0.5616	0.9898	0.1373	0.0373	8.3	0.69
35.	0.08	0.08	0.30	1.0	0.857	1.039	0.4056	0.5971	1.0027	0.1195	0.0395	8.6	0.70
36.		0.20	0.26	1.0	0.817	1.072	0.3861	0.6202	1.0063	0.1005	0.1095	7.5	0.70
37.	0.03	0.15	0.35	1.0	0.821	1.064	0.3881	0.6150	1.0031	0.1110	0.0810	7.7	0.76
38.	0.07	0.06	0.25	1.0	0.761	1.090	0.3604	0.6348	0.9952	0.0999	0.0299	10.1	0.58
39.		0.15	0.34	1.0	0.707	1.145	0.3325	0.6727	1.0053	0.0870	0.0870	8.8	0.69
40.	0.10	0.10	0.20	1.5	1.427	1.455	0.6772	0.8221	1.4993	0.1449	0.0449	8.5	0.68
41.	0.08	0.04	0.36	1.0	0.766	1.092	0.3614	0.6359	0.9973	0.1000	0.0200	10.0	0.68
42.	0.07	0.06	0.36	1.0	0.784	1.100	0.3700	0.6398	1.0098	0.1017	0.0317	8.9	0.70

[a] The value of 232 $M^{-1} cm^{-1}$ for ϵ_I at 329 nm averaged from 183 and 230 $M^{-1} cm^{-1}$ was used for calculation in the $MgCl_2$-$MgSO_4$-Terpyridine TMA mixtures where [TMA] varies from 0.1 to 0.36 M.

in the mixture of $MgCl_2$ and terpyridine free of the TMA salt was used to calculate the results obtained in the $MgCl_2$-$MgSO_4$-terpyridine solutions. As shown in Table A-2, the calculated sums for $[MgI^{+2}]+[I]$ are in excellent agreement with the known total ligand concentrations. Similarly, the extinction coefficients and K_I value obtained including the points having 0.3 M TMA added were used for the $MgCl_2$-$MgSO_4$-terpyridine solution in the presence of 0.11 to 0.36 M TMA salt. Because of some weak interference of TMA with terpyridine and the fact that the TMA concentrations in the $MgSO_4$ solution are not constant, the association constants evaluated are included in Table A-2 for reference only.

A plot of K_{MgSO_4} versus ionic strength in the absence of TMA based on Table A-2 is presented in Figure 3. The best least squares parabola obtained for the curve in Figure 3 is shown as

$$K_{MgSO_4} = 20.901 - 26.802(I_S) + 11.164(I_S)^2 \quad \text{(A-10)}$$

It should be emphasized that equation A-10 is derived on the basis of K_{MgSO_4} values obtained in the experimental ionic strength range from 0.38 to 1.00 M. Therefore, K_{MgSO_4} value at infinite dilution could not be accurately approximated from this equation.

B. *The Ion-Selective Electrode Method :*

The Nernst equation describes the potential response (E) to the ionic activity in solutions as

$$E = E_0 + \frac{RT}{nF} \ln a \quad \text{(B-1)}$$

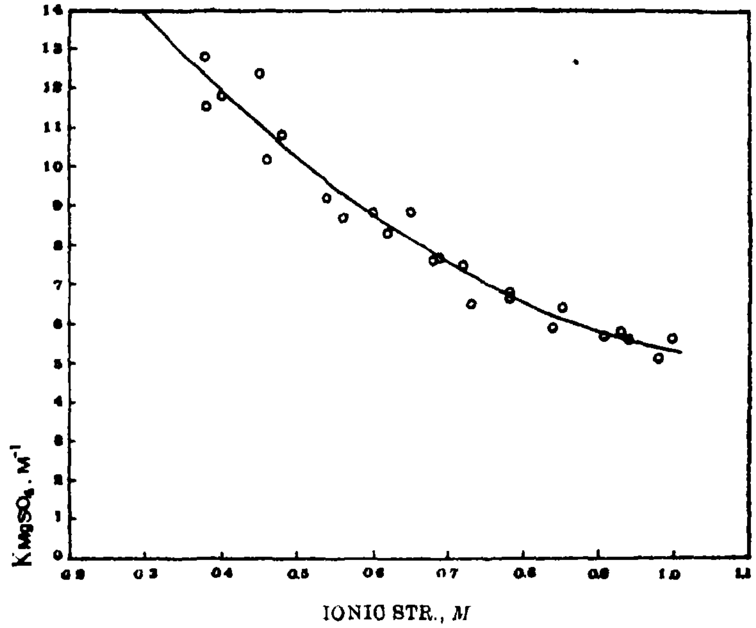


Fig. 3 A Plot of K_{MgSO_4} versus Ionic Strength at 25°C based on Table A-2 absence of TMA. The curve represents the Best Fit.

where E_0 designates the reference electrode potential, R, T, n and F as molar gas constant, absolute temperature, charge on the ion and Faraday constant, respectively. a is the chemical activity of the ion being measured.

Because of their response to ion activity, these electrodes are well suited for ionic association constant determination. In this respect, the electrodes should first be calibrated with standard reference solutions of known activity. Then the activities of test solution can be determined. This technique has been employed to determine the magnesium and calcium ionic concentrations in a seawater model[7]. However, special attention must be given to the experimental procedure in general and in achieving the calibration curve in particular[5,6].

In a pure aqueous $MgSO_4$ solution, the total magnesium concentration, $[Mg]_T$, consists of two parts, free Mg^{+2} and bound ions $MgSO_{4_T}$ as shown in the following reaction.

$$Mg^{+2}(aq) + SO_4^{-2}(aq) \overset{K_{MgSO_4}}{\rightleftharpoons} MgSO_{4_T}(aq)$$

The association constant K_{MgSO_4} is defined in eq. A-7.

To calculate K_{MgSO_4}, the following magnesium concentrations must be known. The total Mg concentration was known from volumetric titration, the free can be determined potentiometrically. The difference in potentiometric measurements between standard, $MgCl_2$ and test solution, $MgSO_4$ can be corrected for using the Nernst slope to obtain the ion activity for the latter. If we assume a value of free Mg^{+2} ion concentration in $MgSO_4$, the ionic strength of the solution can be obtained as a first guess because of the relationship of $I_S = 4[Mg^{+2}]$. Based on this ionic strength, a corresponding activity coefficient is obtained which in turn is used to calculate the magnesium ion concentration from the measured activity. The procedure is iterated several times until the error between the assumed and the calculated magnesium ion concentrations is minimum.

The disadvantage of the present way of calculation to obtain K_{MgSO_4} for both spectrophotometric and potentiometric method is that the measurement errors in Mg^{+2} are multiplied and totally reflected in K_{MgSO_4} value. This is because a smaller than true of Mg^{+2} ion concentration gives rise to a smaller than true $SO_4^=$ and larger than true $MgSO_{4_T}$ concentrations, and vice versa. The results of potential measurements are tabulated in Tables B-1 and B-2. Table B-1 shows a detailed data set for both the standard and test solutions at ten ionic strength. Table B-2 summarizes all the measurements along with the K_{MgSO_4} values calculated from eq. A-10.

The measurement values determined by the two techniques as shown in Figure 4, show that they are in good agreement between 0.3 and 0.6 M ionic strength and in fair agreement between 0.6 and

TABLE B-1—EXPERIMENTAL RESULTS OF A SINGLE MEASUREMENT AT 25°C FOR $MgSO_4$ AND $MgCl_2$ SOLUTIONS

$MgSO_4$ M	$MgCl_2$ M	mv Mg^{++}	$^aMg^{++}$ $M\times10^4$	γ Mg^{++}	Mg^{++} $M\times10^4$	I_s M	K M^{-1}
0.049_6		21.2	11.2_0	0.40_7	27.5_8	0.110	29.1
	0.025_6	21.2	11.2_6	0.44_9	25.3_6	0.076	
0.099_0		26.4	17.2_0	0.34_9	49.8_0	0.197	20.5
	0.048_7	27.8	18.5_0	0.38_0	48.8_7	0.146	
0.148_8		67.5*	23.0_9	0.30_9	74.4_0	0.297	13.4
	0.060_4	66.7	21.7_0	0.35_9	60.4_6	0.181	
0.148_8		32.1	22.0_0	0.31_6	69.7_0	0.279	16.2
	0.060_4	32.0	21.8_0	0.36_0	60.4_6	0.181	
0.198_0		68.9*	26.2_0	0.29_8	89.6_5	0.358	13.5
	0.075_0	68.2	26.2_0	0.33_8	75.0_0	0.225	
0.297_0		71.9*	34.8_0	0.26_7	130.3_0	0.520	9.8
	0.119_8	72.5	35.0_0	0.29_8	119.9_0	0.359	
0.396_0		67.7*	41.0_0	0.25_9	158.3_0	0.683	9.5
	0.159_8	69.2	46.0_5	0.28_8	159.9_0	0.479	
0.496_0		75.9*	46.6_8	0.25_8	185.8_8	0.741	9.0
	0.158_0	75.5	42.4_0	0.26_8	158.0_0	0.574	
0.590_0		77.8*	50.0_0	0.25_0	200.0_0	0.800	9.8
	0.169_8	76.6	45.4_1	0.26_8	169.6_0	0.588	

* In this case the solution used for the reference electrode was not the standard Orion solution, but was 3.3M KCl saturated with $AgNO_3$ as recommended in the Orion Manual when higher ionic strength solutions are measured.

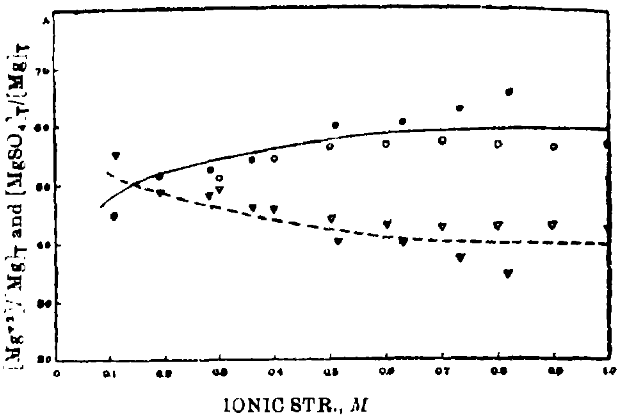


Fig. 4. Plots of $[Mg^{++}]/[Mg]_T$ and $[MgSO_4]_T/[Mg]_T$ versus Ionic Strength at 25°C.
$[Mg^{++}]/[Mg]_T$: ▼, Electrode measurement and ▽, Spectrophotometric measurement.
$[MgSO_4]_T/[Mg]_T$: ●, Electrode measurement and ○, Spectrophotometric measurement. The Electrode data used for calculations are those shown in the first column of Table B-2.

TABLE B-2—A SUMMARY OF K_{MgSO_4} AT 25°C

I_s, $M^{a,b}$	K, M^{-1a}	K, M^{-1c}
0.109	30.0 ± 3.0	—
0.193	22.0 ± 2.0	—
0.285	15.4 ± 1.5	—
0.300		(13.9)[d]
0.361	13.2 ± 2.0	(12.7)[d]
0.400		12.0
0.500	-	10.3
0.512	11.7 ± 1.8	10.1
0.600		8.8
0.682	9.6 ± 0.4	8.4
0.700	-	7.6
0.783	9.3 ± 0.5	7.3
0.800	—	6.6
0.816	9.4 ± 0.5	6.5
0.900		5.8
1.000		5.3

a = Electrode determinations
b = Mean values.
c = Calculated values based on eq. A-10 at the corresponding ionic strength. The errors are generally ±10% or less.
d = Extrapolated value.

0.8 M within the experimental errors. Part of the deviation at ionic strength higher than 0.6 M may reflect the errors involved in the liquid junction potentials inherent in the potentiometric measurements at higher ionic strength[9]. A closely matched free magnesium activity between the standards, $MgCl_2$, and the test solutions, $MgSO_4$, will result in a higher ionic strength for the latter as shown in Table B-1. This part of errors may be sufficiently eliminated if magnesium m-benzene-disulfonate are used as standards. The value of 10.2±0.5 M^{-1} at 0.7 M reported by Pytkowicz *et al*[7c] shows 10-20% higher than the values of this work. The thermodynamic stability constants may be obtained provided appropriate activity coefficients are available.

The activity coefficients at 0.7 M using the data collected by Harned and Owen are 0.36 for $\gamma_{Mg^{++}}$ and 0.12 for $\gamma_{SO_4^{--}}$, respectively[10]. Using these values for extrapolation, the thermodynamic association constant averaged from the spectrophotometric and potentiometric measurements is 196± 19 M^{-1}. This value falls within the range of literature values which are between 129 and 240 M^{-1} [12]. The activity coefficients found for $MgSO_4$ in seawater are lower than those calculated from ionic strength principle for pure electrolytes[11]. Therefore, they are not applicable in the present case.

The mean activity coefficient at 0.109 M ionic strength may be calculated from the Davies equation,

$$\log \gamma_i = -0.5\, z_i^2 \left[\frac{\sqrt{I_s}}{1+\sqrt{I_s}} - 0.3 I_s\right] \quad \ldots \quad \text{(B-2)}$$

and it is found to be 0.371. This K_{MgSO_4} at infinitive dilution becomes 218±22 M^{-1}. On the basis of equation (B-2), a linear relationship between $\log K_{MgSO_4}$ versus $\sqrt{I_s}$ is expected at ionic strength to be lower than 0.01 M. The results of these studies will be corporated with those of $CaSO_4$ association reactions and presented elsewhere[8].

Acknowledgement

The work was supported by the Office of Naval Research under Grant number N00014-72-0285-0001.

The authors are grateful to Dr. Gordon Atkinson for helpful discussions.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 884-886

Extraction and Spectrophotometric Determination of Vanadium(V) with N-Hydroxy-N-*p*-Chlorophenyl-N′-(3-chloro-4-methyl) phenylbenzamidine**

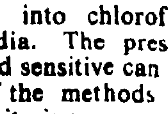
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Manuscript received 26 March 1979, revised 30 July 1979, accepted 9 July 1980

A highly selective spectrophotometric method has been developed for the determination of vanadium(V) at ppm level. A chloroform solution of N-hydroxy-N-p-chlorophenyl-N′-(3-chloro-4-methyl)phenylbenzamidine quantitatively extracts vanadium(V) as blue-violet complex from 0.5-10.0*M* acetic acid media. The complex shows a broad absorption maxima at 570-590 nm having the value for molar absorptivity to be 4210 l.mole^{-1}cm^{-1}. The sensitivity of the colour reaction is 0.011 μg of vanadium(V) cm^{-2}. The 1 : 2 (vanadium : reagent) complex adheres to Beer's law in the range 20 μg to 300 μg/25 ml. The influence of various experimental factors such as time, temperature, concentration of the reagent and the presence of diverse ions, etc. have been studied.

SINCE the introduction of N-hydroxy-N, N′-diphenylbenzamidine as a new class of organo-analytical reagent by Satyanarayana and Mishra[1], several analogous compounds have been synthesised[2] and applied for the gravimetric and spectrophotometric determination of a number of transition metal ions[3-5]. As compared to the established reagents such as cupferron, N-benzoylphenylhydroxylamine, α-benzoinoxime, 8-hydroxyquinoline[6] and 3-hydroxy-1, 3-diphenyl triozene[7], the hydroxyamidine functional grouping I, provides wider scope as due to great synthetic flexibility, substitution at all the three available sites can be made with a view to modifying the complexing property of the reagent



I

The newly synthesised reagent, N-hydroxy-N-*p*-chlorophenyl-N′-(3-chloro-4-methyl)phenylbenzamidine has been employed for the highly selective spectrophotometric determination of vanadium(V) after extraction into chloroform from 0.5-10.0*M* acetic acid media. The present method, which is simple, rapid and sensitive can be compared favourably with any of the methods for vanadium(V)[8-9] so far as selectivity is concerned.

Experimental

Apparatus : An ECIL UV-VIS spectrophotometer GS-865 equipped with 1 cm matched quartz and silica cells was employed for absorbance measurements.

Standard vanadium(V) solution : A stock solution of vanadium(V) was prepared by dissolving ammonium meta vanadate (BDH. A.R.) in double distilled water. The vanadium content of this solution was determined volumetrically[10].

Preparation of N-hydroxy-N-p-chlorophenyl-N′-(3-chloro-4-methyl)phenylbenzamidine :

The reagent was prepared by the condensation of equimolar quantities of N-(3-chloro-4-methyl)-phenylbenzimidoyl chloride and N-*p*-chlorophenyl hydroxylamine in ether medium[2]. The resulting hydrochloride was filtered and treated with dilute ammonia to get the free base. The pale-yellow crystals of the reagent were obtained upon crystallisation from petroleum ether : benzene (1 : 2) mixture. m.p. 168-169°, yield : 50%. (Found : C, 64.50 ; N, 7.38 ; H, 4.48 percent. Calcd. for $C_{20}H_{16}N_2OCl_2$; C, 64.69 ; N, 7.54 ; H, 4.31 percent.) A 0.1% W/V solution of the reagent in chloroform was employed for extraction purposes.

Procedure : Place an aliquot of the solution containing 100 μg of vanadium(V) in a 60 ml separating funnel. To this add required amount of acetic acid (so adjust the acidity between 0.5-10.0 *M*) and sufficient water to bring the total volume to 25 ml. Add 10 ml of chloroform solution of the reagent and shake vigorously for 1 min, separate the coloured chloroform layer containing the vanadium complex and collect over anhydrous

**Presented at the Annual Convention of Chemist, 1978 held at Waltair

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sodium sulphate in a small beaker. Extract the aqueous phase with 2 × 4 ml portions of chloroform and mix with the main extract. Transfer the combined extracts into a 25 ml volumetric flask and dilute to volume with chloroform. Measure the absorbance at 580 nm against chloroform as blank.

Results and Discussion

Absorption spectra : The absorption spectra of vanadium(V)-HCPCMPB complex and reagent are shown in Fig. 1. The vanadium-HCPCMPB complex show λ_{max} at 580 nm with ϵ, 4210 l. mole^{-1} cm^{-1} (in 0.5-10.0 *M* acetic acid). The reagent has negligible absorbance in the region 450-700 nm.

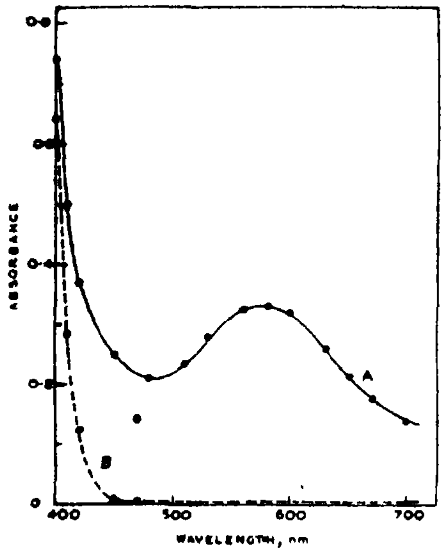


Fig. 1. Absorption Spectra :

(A) (-⊙-○-⊙-) 4 ppm Vanadium + 0.008*M* HCPCMPB in chloroform.

(B) (-●-●-●-) 0.008*M* HCPCMPB in chloroform

Effect of variables : The acidity was maintained with glacial acetic acid and optimum acidity range was found to be 0.5-10.0 *M* acetic acid. A 7 fold molar excess of reagent was adequate for complete extraction of vanadium(V). Addition of excess reagent had no adverse effect. Order of addition of reagent was not critical.

A time of 1 min. was sufficient for complete extraction of vanadium(V). Variation in temperature from 20 to 35° and aqueous phase from 10-60 ml did not affect the position of absorption band and absorbance of coloured system.

Beer's law, optimum concentration range, molar absorptivity and precision : The system obeyed Beer's law upto 0.8 to 12.0 ppm. The optimum concentration range on the basis of Ringbom[11] plot was found to be 2.8 to 10 ppm. The effective molar absorptivity was 4210±50 l. mole^{-1} cm^{-1} with a Sandell's[12] sensitivity 0.011 μg metal per cm^2.

The mean absorbance value of 15 samples each containing 4 ppm of vanadium(V) was found to be 0.33 at 580 nm. The standard and relative standard deviations were $\pm 3.27 \times 10^{-3}$ absorbance unit and ±0.99% respectively.

Composition : In V(V)-HCPCMPB complex, the ratio of vanadium to reagent was determined by molar ratio[13], slope ratio[14] and Job's method of continuous variations[15]. The results obtained showed the formation of 1 : 2 (metal : reagent) complex in chloroform.

TABLE 1—TOLERANCE LIMIT OF DIVERSE IONS IN THE DETERMINATION OF 4 ppm VANADIUM(V) AT 6*M* ACETIC ACID

Ions added	Tolerated* amount ppm	Ions added	Tolerated* amount ppm
Fe^{3+}	800	Ti^{4+}	60
Cu^{2+}	500	Mo^{6+}	300
Co^{2+}	700	W^{6+}	20
Ni^{2+}	700	Al^{3+}	600
Zn^{2+}	1000	Cr^{3+}	600
Cd^{2+}	1000	Tl^{3+}	800
Mn^{2+}	800	Th^{4+}	800
Pb^{2+}	1200	Arsenate	400
Ag^{+}	700	Citrate	600
Sb^{3+}	600	Tartrate	600
Nb^{5+}	100	Fluoride	500
Ta^{5+}	200	Iodide	600

* error causing 2%.

Effect of foreign ions : The effect of foreign ions for determination of 4 ppm vanadium(V) was studied at 6 *M* acetic acid concentration of the aqueous phase. Varying amount of the foreign ions were taken with a fixed amount of vanadium and the colour was developed and measured as described in earlier procedure.

Chloride, bromide, nitrate, sulphate, ammonium, phthalate, borate, triethanolamine, lanthanoid elements, alkaline and alkali-earth elements did not interfere upto 2000 ppm. The tolerance limits of other ions are shown in Table 1.

Application of method in B. C. S. Steels :

The validity of method was tested in two tungsten steels 64a, 241/1 and tungsten free vanadium steel 252 obtained from the Bureau of Analysed Samples, Ltd., Newham Hall, Middlesbrough, Yorks.

The results obtained are shown in Table 2.

TABLE 2—DETERMINATION OF VANADIUM IN B.C.S.* STEELS

Name of steel	Vanadium[a] found	Certified value	Standard deviation
64a Alloy steel	1.567	1.57	±0.01058
241/1 High speed steel	1.56	1.57	±0.00648
252 Low alloy steel	0.454	0.46	±0.00845

* British Chemical Standards
a Average of 5 determinations.

A weighed quantity of sample containing 3 mg of vanadium was dissolved in dilute nitric acid (30%). The hydrated tungstic oxide was filtered through Whatmann filter paper No. 42. The oxides of nitrogen were removed by boiling and vanadium content of sample was determined by the recommended procedure.

Acknowledgement

The authors are thankful to Dr. S. G. Tandon, Head, Dept. of Chemistry, Ravishankar University, Raipur, for providing research facilities and to the Council of Scientific and Industrial Research, New Delhi for the award of a fellowship to one of them (PKS).

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 887-889

Analytical Applications of 3-Anilino-2-Thiotetrahydroquinazole-4-One (ATQ-4-O) I-Spectrophotometric Determination of Palladium(II)

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3-Anilino-2-thiotetrahydroquinazole-4-one (ATQ-4-O) is synthesised and use of its Pd(II)-complex in the spectrophotometric determination of metal is explored. Pd(II)-ATQ-4-O complex absorbs maximum at 370 (ε 8400) and 380 nm (ε 10700) respectively in 60% acetone and chloroform media. Composition of the complex is 1 : 2 (metal : ATQ-4-O) in both the media. Accurate conditions for micro-determination of palladium in 60% acetone and by extractive procedure are developed. Study of diverse ion effect reveals that large quantities of other ions including platinum-metals (except osmium) either do not interfere or can be masked with suitable masking agents. Extractive procedure is more selective and sensitive. ATQ-4-O is more sensitive than pyrimidine-2-thiols.

SEVERAL heterocyclic thiols have been investigated for the spectrophotometric determination of the platinum-metals by Singh and co-workers[1-7]. Among them 1-substituted pyrimidine-2-thiols are most promising reagents for the selective determination of palladium(II)[1-8]. In continuation of these studies a new heterocyclic thiol 3-anilino-2-thiotetrahydroquinazole-4-one (ATQ-4-O) is synthesised and examined for analytical purpose. Of the platinum metals it reacts with palladium(II) and osmium(VIII) in cold (acidic medium) forming intense coloured complexes suitable for their spectrophotometric determination. Other platinum metals react with this ligand on prolonged heating. Due to this reason large amounts of all other platinum-metals except osmium are tolerable in the photometric determination of palladium. This is similar to what is observed with pyrimidine-2-thiols—a higher selectivity for palladium. In the present communication results of investigations on complexation of ATQ-4-O with palladium(II) carried out with a view to establish optimum conditions for determination of the metal spectrophotometrically are reported.

Experimental

Synthesis of ligand (ATQ-4-O) :

It involves two steps. In the first phase 6-aminobenzoyl-β-phenyl hydrazide is obtained from isatoic anhydride, which is converted into 6-anilino-2-thiotetrahydro quinazole-4-one by reaction with carbon disulphide in the second step. Details of both reactions are as follows :

6-Aminobenzoyl-β-phenylhydrazide :

Isatoic anhydride (16.5 g ; 0.1 mole) and phenylhydrazine (10.8 g ; 0.1 mole) dissolved in ethanol (50 ml) were refluxed on a water bath. The evolution of carbon dioxide which started immediately, abated in about two hr. It was refluxed further for about 1 hr. Solvent was removed under vacuum and the compound thus precipitated was recrystallised from ethanol. The m.p. was 169-170° and yield 18.2 g (80%). Calculated C, 68.73% ; H, 5.72% : N, 18.83% ; found C, 69.0% ; H, 5.64% ; N, 18.23%.

3-Anilino-2-thiotetrahydroquinazole-4-one :

Sodium hydroxide (2.4 g ; 0.06 mole) dissolved in water (10 ml) was added to a cooled solution of 6-aminobenzoyl-β-phenylhydrazide (11.35 g ; 0.05 mole) and CS_2 (7.6 g ; 0.1 mole) in ethanol (50 ml) in a 250 ml conical flask. The flask was stoppered and left overnight on a magnetic stirrer. The mixture was diluted with water (50 ml) and made acidic with acetic acid. The precipitated compound was filtered, washed with water and dried. After final recrystallisation from glacial acetic acid its m.p. was 236-238° and yield 12.0 g (90%). Calculated C, 62.44% ; H, 4.09% ; N, 15.61% ; Found C, 62.13% ; H, 4.15% ; N, 15.73%.

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Preparation of solutions :

Standard solution of Pd(II) was prepared by dissolving anhydrous $PdCl_2$ (Johnson Mathey) in 1 *M* hydrochloric acid. It was standardised gravimetrically before use[8]. Ligand solutions were prepared by dissolving appropriate amounts in chloroform (0.005 *M*) and in acetone (0.01 *M*). All other chemicals used were of reagent grade. Doubly distilled water was used throughout the work.

Apparatus :

UV and visible spectra of ligand and its palladium(II)-complex were recorded with Cϕ-16 Russian spectrophotometer. IR spectrum in Nujol mulls of ligand was recorded on Perkin-Elmer 521 model IR spectrometer.

Procedure for determination in 60% acetone :

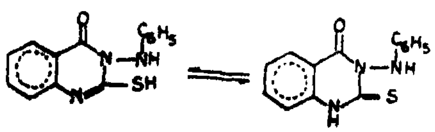
To a suitable aliquot containing 10-80 μg of palladium(II) add sufficient amount of concentrated HCl, so that in final solution acid concentration (in 10 ml) is in the range 2-4 *M*, and 3 ml of 0.01 *M*, ATQ-4-O solution in acetone. Make up the volume to 10 ml, keeping 60% acetone (V/V) in the medium and measure its absorbance, at 370 nm against reagent blank. Determine the metal content from calibration curve.

Extractive procedure :

Take a solution containing 20-70 μg of palladium in separating funnel. Add to it 2-6 ml of 10 *M* HCl and make up the volume to 10 ml. Shake this solution with 10 ml of 0.005 *M* ATQ-4-O in chloroform for about 15 min. Separate the organic phase and measure its absorbance at 380 nm against reagent blank. Calculate the palladium contents from precalibrated graph.

Results and Discussion

ATQ-4-O can exist in thiol(I) as well as in thione(II) form. However the IR spectrum of solid compound does not have band in 2500-2600 cm^{-1} region. This indicates that ligand does not contain



I ⇌ II

free –SH group in the solid state although it may behave as thiol in solution. The presence of a sharp but very weak band at 2470 cm^{-1} indicates that the proportion of hydrogen bonded thiol is also very small in solid state than the concentration of thione form. Occurrence of thioamide bands I, II, III and IV[9-11] at 1530, 1295 (m), 960 (m) and 740 cm^{-1} (m) respectively further supports the existence of thione form in solid state.

Complexation reaction with Pd(II) :

Addition of colourless solution (λ_{max} 328 nm) of ATQ-4-O in acetone to palladium solution in presence of hydrochloric acid results in the formation of golden-yellow colour (stable for 24 hr). Ligand as well as its Pd(II) complex precipitates if acetone contents are lowered below 50%. Thus studies on palladium(II) complex have been made in 60% (V/V) acetone medium. Alternately on shaking the acidic palladium(II) solution with ligand solution in chloroform, the metal ion passes as golden-yellow complex into organic phase. Extraction into carbon tetrachloride, *n*-butanol and benzene is also possible but absorbance values have been found to be lower in these media. Chloroform is thus chosen for extraction. Complexation reaction in both media is investigated with a view to explore its applicability for palladium determination. Optimum conditions for determination are established and effect of diverse ions is investigated for both procedures. Results are described below

Palladium(II)-ATQ-4-O complex system in 60% acetone medium :

Yellow coloured palladium-ATQ-4-O complex absorbs maximum at 370 nm (ϵ = 8400 l $mole^{-1}$ cm^{-1}) in the 60% acetone medium. Effect of acid concentration on complexation is studied. The absorbance is maximal and constant in 2.0-4.0 *M* hydrochloric acid. Other mineral acids can also be used in place of HCl For full colour development at least 25-fold excess of ligand over metal is required. Further excess does not affect the absorbance. Beer's law is obeyed upto 12.5 ppm of palladium. The Sandell's sensitivity of the reaction is 0.0125 μg/cm^2. From Ringbom plot optimum concentration range for determination has been found to be 1-8 ppm. The relative standard deviation is ±0.96%. Metal to ligand ratio in complex has been found to be 1 : 2 by Job's and logarithmic methods.

Palladium(II)-ATQ-4-O complex in chloroform :

The extracted Pd-ATQ-4-O complex in chloroform absorbs maximum at 380 nm. The extraction efficiency is 99.5% in the presence of 2-6*M* hydrochloric acid and 20-fold molar excess of ligand. Further excess of ligand does not affect the efficiency. Sulphuric, phosphoric, perchloric and nitric acids are also equally good for extraction purpose. Shaking for 10 min on electrical shaker is sufficient for complete extraction. Beer's law is obeyed upto 10 ppm of metal. Accurate concentration for determination is 2-7 ppm of palladium. The relative standard deviation is ±0.82%. The

values of molar extinction coefficient and Sandell's sensitivity are 10700 mole^{-1} cm^{-1} and 0.01 μg/cm^2 respectively. Composition of the complex in this medium has also been found to 1 : 2 (metal : ligand).

Effect of diverse ions :

Effect of diverse ions in the determination of 6 ppm of palladium is investigated. I^-, CN^-, SCN^-, $S_2O_3^{2-}$ and thiourea interfere seriously in both media. Tolerance limits (with error of $\pm 2\%$ in absorbance) for other ions are incorporated in Table 1. Improvement in the tolerance limits for numerous cations is done with the use of suitable masking agent. Improved values are given in Table 2. Comparison of ATQ-4-O with pyrimidine-2-thiols[1-6] reveals that it is more sensitive and comparable in selectivity. However, the extractive procedure is more selective than the other one.

TABLE 1—TOLERANCE LIMITS FOR DIVERSE IONS

Foreign ion	Tolerance limit (ppm)	
	in 60% acetone medium	in extractive procedure
F^- or Br^-	2000	5000
NO_2^-	50	100
NO_3^-	5000	5000
CH_3COO^-	2000	5000
SO_4^{2-} ; SO_3^{2-}	5000 ; 1000	5000 ; 2000
$C_2O_4^{2-}$	1500	3000
Tartrate	2000	3000
PO_4^{3-} ; BO_3^{3-}	5000 ; 2000	5000 ; 4000
Citrate	1000	3000
EDTA	1000	3000
Ca^{2+} or Sr^{2+} or Ba^{2+}	1000	3000
Zn^{2+} or Cd^{2+}	50	400
Sn^{2+} ; Hg^{2+}	40 ; 20	100 ; 50
Mn^{2+} ; Cu^{2+}	60 ; 5	1000 ; 25
Al^{3+} ; V^{4+}	80 ; 10	1000 ; 25
Ru^{3+} ; Rh^{3+}	40 ; 40	200 ; 200
Ir^{3+} ; Pt^{4+}	40 ; 20	200 ; 180
Ag^+ ; Au^{3+}	10 ; 10	50 ; 20
Os^{8+}	5	5
Fe^{2+} or Fe^{3+}	10	20
Co^{2+} ; Ni^{2+}	15	25

TABLE 2—IMPROVED TOLERANCE LIMITS FOR CATIONS IN PRESENCE OF MASKING AGENTS

Cations	Tolerance limits (ppm)		Masking agent
	in 60% acetone medium	in extractive procedure	
Cu^{2+}	25	500	EDTA or Citrate
Co^{2+}	50	700	EDTA
Ni^{2+}	50	600	EDTA or Citrate
Fe^{3+}	40	500	Fluoride
Al^{3+}	200	2000	Fluoride
Hg^{2+}	50	200	Citrate or Tartrate or EDTA
Sn^{2+}	100	250	Fluoride
Zn^{2+}	200	1000	Citrate or EDTA or Tartrate
Cd^{2+}	150	850	EDTA or Tartrate
Rh^{3+}	75	400	EDTA or Citrate

Further studies on analytical applications of ATQ-4-O are in progress and will be reported in subsequent parts of this series.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 890-892

Titrimetric Determination of Certain Organic Compounds by Oxidation with Alkaline Potassium Permanganate

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Manuscript received 25 May 1979, revised 6 March 1980, accepted 9 July 1980

A titrimetric procedure has been described for the determination of cinnamic, cyanoacetic, pyruvic and ascorbic acid, mannitol, thiourea and allylthiourea based on their oxidation at ordinary temperature with alkaline permanganate in presence of barium ions. In some cases nickel nitrate has been used as a catalyst. The effect of variation in the different factors influencing the stoichiometry of these oxidation reactions has also been investigated. The proposed method can be adopted for determining 0.01-0.1 *M* solution of these compounds with an accuracy of $\pm 0.8\%$ or better.

POTASSIUM permanganate is capable of oxidizing several organic compounds but the rate of oxidation is usually slow. This is a major problem in developing oxidimetric procedures for estimating organic compounds using permanganate as oxidant. The oxidation rate can be enhanced by heating the reaction mixture but then the autodecomposition of permanganate becomes quite appreciable and vitiates the accuracy of the method. According to Kolthoff[1], the oxidation of an organic substance proceeds more rapidly in alkaline medium than in acid. Imhof[2] achieved the complete oxidative breakdown of a number of organic compounds by utilizing oxidising power of permanganate both in alkaline and in acid solution but the time required for the completion of the reaction was 26 hrs.

The proposed procedure which requires only 15-30 mins for quantitative oxidation, is based on the following considerations. During the oxidation of organic compounds, in a fairly strong alkaline medium, permanganate gets reduced to manganate which is further reduced to manganese dioxide in the second step. This secondary reduction renders the oxidation reaction unsuitable for application in quantitative analysis. In presence of barium ions, the insoluble barium manganate is formed and hence the secondary reaction involving the formation of manganese dioxide scarcely proceeds at all[3]. On the basis of this fact a direct volumetric method has been evolved for determining certain organic compounds using alkaline permanganate at room temperature as oxidant. The time required for the completion of the reaction is shortened considerably when barium chloride is added to the reaction mixture[4]. Several sets of experiments were conducted to study the effect of change in the amount of sodium hydroxide, barium chloride, nickel nitrate and of the time on the stoichiometry of the oxidation of the organic substances tested. After critically evaluating the results of these experiments, appropriate experimental conditions, leading to quantitative oxidation, were ascertained ; these have been recorded in Table 1.

Experimental

Sodium oxalate and potassium permanganate were of A.R. grade. 0.1 *M* permanganate solution was prepared and standardised with sodium oxalate[5]. Saturated solution of barium chloride was prepared from B.D.H. product. 0.25, 0.1 and 0.05% solutions of nickel nitrate and 10 *M* sodium hydroxide solution were prepared using E. Merck's variety. Since the solubility of cinnamic acid in water is poor, 0.1 *M* solution of its sodium salt was prepared and standardised by Imhof's method[2]. 0.1 *M* cyanoacetic acid was prepared and standardised by alkalimetry. Pyruvic acid solution was also standardised by Imhof's method. Ascorbic acid solution was standardised by titration with potassium iodate solution in presence of potassium iodide and sulphuric acid[6]. Hypoiodite oxidation method was applied for standardising thiourea[7].

In titrating an alkaline solution of permanganate with the solution of the organic substance to be determined, the difficulty is that if titration is done rapidly, more volume of reductant solution is required than required theoretically owing to incomplete reaction. On the other hand, if too much time is allowed during the titration, the volume of titrant is less than the stoichiometric value due to autodecomposition of permanganate. This difficulty has been circumvented by adopting the following procedure.

Procedure :

25 ml of 0.1 *M* potassium permanganate solution is pipetted into an Erlenmeyer flask and amounts of

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TABLE 1

(25.0 ml of 0.1 *M* POTASSIUM PERMANGANATE TAKEN FOR TITRATION)

Compound	$Ni(NO_3)_2$ added (ml)	10 *M* NaOH added (ml)	Satd. $BaCl_2$ added (ml)	Total titration time (mins)	No. of equiv. used per mole of reductant	Mg of substance 1 ml of 0.1 *M* $KMnO_4$ soln
Cinnamic acid	2.6-2.8 (2.7 of 0.05%)	3-10 (5.0)	7-12 (8.0)	12-18 (15)	10	1.4815
Cyanoacetic acid	—	2-14 (5.0)	7-12 (8.0)	10-20 (15)	6	1.4176
Pyruvic acid	1.9-2.1 (2.0 of 0.05%)	4-8 (5.0)	6-10 (8.0)	15-20 (15)	10	0.8806
Ascorbic acid	1.5-1.8 (1 6 of 0.25%)	3-6 (4.0)	8-13 (10.0)	14-18 (15)	20	0.8806
Mannitol	2.6-3.0 (2.8 of 0.1%)	4-10 (5.0)	7-13 (10.0)	12-18 (15)	26	0.7007
Thiourea	—	3-8 (5.0)	7-12 (10.0)	15-22 (20)	12	0.6348
Allylthiourea	--	5-15 (10.0)	6-12 (10.0)	32-40 (35)	26	0.4468

Recommended volumes of nickel nitrate, sodium hydroxide and barium chloride solution are given in parentheses. When the volume of permanganate taken for titration is different from 25 ml, the volumes of alkali, barium chloride and nickel nitrate solutions are changed proportionately.

TABLE 2

Compound	0.1 *M* permanganate used for titration (ml)	Solution used for titration (*M*)	Titre Theoretical	Titre Obtained	% Error
Cinnamic acid	25.0	0.05	5.0	5.0	Nil
	25.0	0.0166	15.0	15.1	−0.7
	25.0	0.0125	20.0	20.1	−0.5
Cyanoacetic acid	25.0	0.05	8.33	8.34	−0.1
	25.0	0.025	16.66	16.6	+0.4
	10.0	0.00625	26.66	26.8	−0.5
Pyruvic acid	50.0	0.1	5.00	4.96	+0.8
	25.0	0.025	10.00	10.03	−0.3
	25.0	0.0125	20.00	20.1	−0.5
Ascorbic acid	25.0	0.025	5.00	4.96	+0.8
	25.0	0.0125	10.00	10.00	Nil
	25.0	0.00625	20.00	20.2	−1.0
Mannitol	25.0	0.025	3.85	3.84	+0.3
	25.0	0.0125	7.69	7.70	−0.2
	25.0	0.00625	15.4	15.5	−0.7
Thiourea	50.0	0.1	4.17	4.19	−0.5
	25.0	0.025	8.33	8.34	−0.2
	25.0	0.0125	16.7	16.80	−0.7
Allylthiourea	25.0	0.025	8.85	8.86	−0.3
	25.0	0.0125	7.70	7.76	−0.8

Note : Microburette was used whenever titre was less than 10 ml.

sodium hydroxide, barium chloride and nickel nitrate as shown in Table 1 are added. The reaction mixture is heated to about 80° and titrated in 2-4 minutes with the sample solution to be determined. The approximate titre so obtained is noted. This hot titre is slightly less than the theoretical value because autodecomposition of permanganate increases with rise in temperature.

The same reaction mixture is taken and the volume of the titrant corresponding to the hot titre (as determined above) is added all at once. The mixture is kept for about 10-12 mins during which it should be frequently shaken. The titrant is then added dropwise slowly with thorough shaking till the permanganate colour disappears. The rate of addition of the titrant is so adjusted that in all about 15 mins are required for the titration. In case of thiourea and allylthiourea the total titration time is 20 mins and 35 mins respectively. If the aforementioned mode of addition of the titrant is followed, the bulk of the reaction gets completed in the initial stage of the titration leaving very little permanganate for autodecomposition in the slow second stage of the titration. Thus, the autodecomposition of permanganate, a major source of error in these titrations, is kept at a minimum. Table 1 gives the range of quantities of nickel nitrate, sodium hydroxide and barium chloride to be added and titration time within which satisfactory results can be obtained.

Results and Discussion

The proposed procedure has been applied for

the determination of seven organic compounds. The analysis has been carried out at three concentration levels, using test solutions between the range 0.1 to 0.01 *M*. The recovery studies as presented in Table 2 show that the maximum error is ±0.8%. Table 1 shows that the quantitative oxidation of the compounds tested can be achieved in 15-30 mins. In these redox reactions, permanganate is reduced to manganate involving only one electron change, hence its equivalent weight is equal to its molecular weight. This relationship coupled with the fact that large number of oxidizing equivalents are consumed per molecule of the compounds studied, makes the proposed method suitable for the quantitative analysis of dilute solutions of these substances.

Acknowledgement

Thanks of the authors are due to the University Grants Commission for the award of fellowship to one of them (S.P.C.).

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 893-897

Vinyl Polymerisation by an Iron Complex

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Manuscript received 1 August 1978, revised 12 May 1980, accepted 9 July 1980

The kinetics of polymerisation of acrylamide, methacrylamide and methyl methacrylate initiated by dichloro *bis*(N-2,5 dihydroxy acetophenacylidene-*p*-dimethylamino anilino) ferrate(III) in DMF medium at $[H^+]=8\times10^{-3}$ *M* was studied at $45\pm0.1°$. The rate of polymerisation was followed gravimetrically and the chainlengths of the polymers were determined viscometrically. There was no polymerisation at $[H^+]<4.2\times10^{-4}$ *M*. The rate of polymerisation was found to be proportional to $[monomer]^{1.4}$ and $[initiator]^{0.4}$. In the case of methacrylamide and methyl methacrylate polymerisations, the initiator exponent was found to be 0.3. The apparent activation energies for the polymerisation reactions have been calculated. A kinetic reaction scheme is proposed on the basis of the experimental data.

STUDIES have been made about the catalytic behaviour of iron complexes towards polymerisation of vinyl monomers[1-6]. Das and George[5] studied the effect of iron(III) chloro complexes on the polymerisation of styrene. Dainton and Jones[6] studied extensively the photopolymerisation of acrylonitrile initiated by iron(III) chloro complexes in DMF medium. In this paper, we present a systematic kinetic study of the polymerisation of acrylamide, methacrylamide and methyl methacrylate initiated by dichloro *bis* (N-2, 5 dihydroxy-acetophenacylidene-*p*-dimethylamino anilino) ferrate (III) in DMF medium at $45\pm0.1°$.

Experimental

Acrylamide, methacrylamide and methyl methacrylate were purified by known procedure. N, N-Dimethyl formamide was allowed to stand over KOH pellets for an hour, then over $CaSO_4$ granules overnight before vacuum distillation. Perchloric acid (E. Merck, G.R., Ca 60% $HClO_4$) was used.

Dichloro *bis*(N-2, 5 dihydroxy acetophenacylidene-*p*-dimethylamino anilino) ferrate(III) was prepared according to the method of Singh and coworkers[7] and its purity was checked by spectrophotometry.

The reaction vessel consisted of a Pyrex test tube (20 cm × 4 cm) fitted with an inlet and an outlet. A thermostated monomer solution, containing the calculated amount of $HClO_4$, was deaerated by bubbling oxygen-free nitrogen through the inlet tube for 30 minutes. After 30 minutes, the complex solution was added through the outlet tube which was then closed with a stopper. There was no induction period and the steady state rate was attained in about 15 minutes.

The viscometric average molecular weight of the polyacrylamide was calculated[8] from the equation.

$$[\eta]=KM^{\alpha}$$

taking $K=6.31\times10^{-5}$, where concentration is in gm/100 ml, η, the intrinsic viscosity, and $\alpha=0.8$. The chainlengths (n) of the poly(methyl methacrylate) samples were determined using the equation given by Baxendale[9], viz., $n=2.81\times10^{3}(\eta)^{1.32}$

Kinetic Scheme :

For the iron complex, the possible reactions involved in polymerisation can be represented as follows. The monomer formed an adduct with the iron complex which decomposed in the presence of acid to give the monomer radical, $M^{\cdot}$.

$$M+C\overset{K}{\rightleftharpoons}[M-C] \quad \ldots (1)$$

$$[M-C]+H^{+}\xrightarrow{k'_1}M^{\cdot}+Fe(II) \quad \ldots (2)$$

where C was the complex and [M − C], the adduct. Such type of complex formation between the monomer and the complex was also proposed by Delzenne[10] in explaining the second order dependence of the rate of polymerisation of acrylamide by aquopentammine cobalt(III). That the iron complex decomposed in presence of acid to gives Fe(II) species was supported by the disappearance of the absorption band at 20,000 cm^{-1} and appearance of a new band at 28,000 cm^{-1} [11] (Fig. 1).

Propagation of polymerisation :

$$M^{\cdot}+M\xrightarrow{k_p}M^{\cdot}_2 \quad \ldots (3)$$

$$M^{\cdot}_{n-1}+M\xrightarrow{k_p}M^{\cdot}_n$$

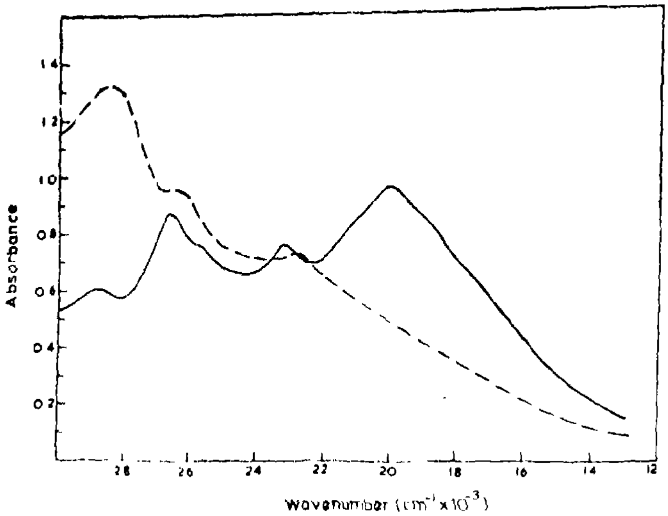


Fig. 1. Absorption spectrum of the Iron Complex 8.3×10^{-4} M solution in DMF.

— , in the absence of acid

...., in the presence of acid.

Termination of polymerisation :

$$M^{\cdot}_n + M^{\cdot}_m \xrightarrow{k_{t_1}} M_{n+m} \quad \ldots (4a)$$

$$M^{\cdot}_n + [C] \xrightarrow{k_{t_2}} \text{Polymer} \quad \ldots (4b)$$

$$M^{\cdot}_n + M^{\cdot}_m \xrightarrow{k_{t_3}} M_n + M_m \quad \ldots (4c)$$

Transfer reactions to the initiator leading to inactive products can also be considered

$$M^{\cdot}_n + [C] \xrightarrow{k_{t_r}} \text{Products} \quad \ldots (4d)$$

Termination by the primary radical, in this particular case is not different from termination by mutual combination. Since it is well known that many initiator systems form a complex with the monomer molecule, where the complex species functions as the initiator, the initiating radical is kinetically indistinguishable from the propagating radical. In orthodox systems like benzoylperoxide initiated system, the initiator decomposes in the initiation step to give a primary radical, viz., benzoyloxy radical which is different from the propagating radical viz., $M^{\cdot}_n$. In such cases, termination by primary radicals would lead to a rate expression independent of the initiator concentration. Assuming stationary state kinetics for $M^{\cdot}$ and $M^{\cdot}_n$, and that termination by mutual combination takes place, the rate expression can be derived to be

$$R_p = k_p\left[\frac{Kk_i}{k_{t_1}}\right]^{\frac{1}{2}}[H^+]^{\frac{1}{2}}[C]^{\frac{1}{2}}[M]^{3/2} \quad \ldots (5)$$

Assuming termination by complex molecule, the rate expression would be

$$R_p = k_p\left[\frac{Kk_i}{k_{t_2}}\right][H^+][M]^2 \quad \ldots (6)$$

If transfer reactions and mutual combinations are taking place, the rate expression would be

$$R_p = 2\left[\frac{Kk_i}{k_{t_r}}\right]k_p[M]^2[H^+] \quad \ldots (7)$$

Results and Discussion

Free radical nature of the polymerisation is evident from the fact that polymerisation is inhibited by hydroquinone and retarded effectively by atmospheric oxygen.

The influence of monomer concentration on the rate of polymerisation was studied over a 10 fold concentration range in the case of acrylamide and a 7 fold concentration range in the case of methacrylamide and methyl methacrylate. The plot of R_p versus $[M]^{1.5}$ (Fig. 2) was a straight line passing through the origin indicating that the rate of polymerisation was 1.5 order in monomer concentration. This indicated the participation of the monomer in the initiation of polymerisation.

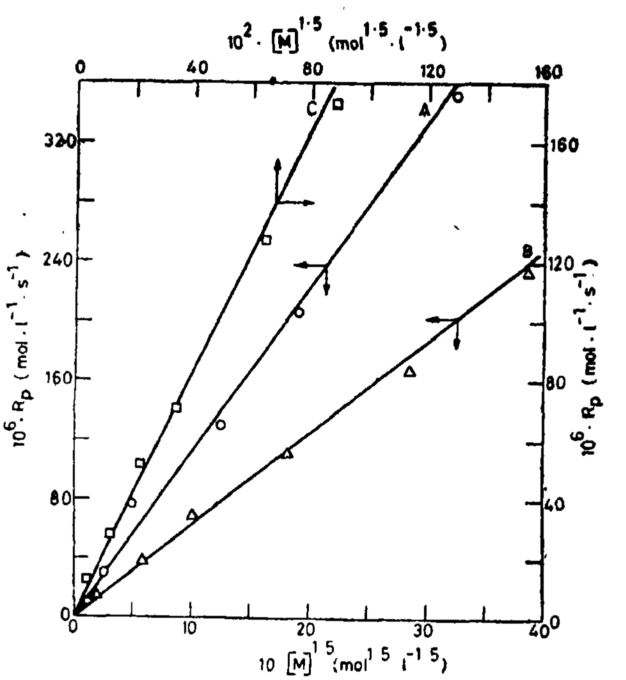


Fig. 2. Plot of rate of polymerisation versus monomer concentration at 45°C.
[Complex] = $4.768\times10^{-5} M$ [$HClO_4$] = $8\times10^{-3} M$
A. *Acrylamide*
B. *Methacrylamide*
C. *Methyl methacrylate*

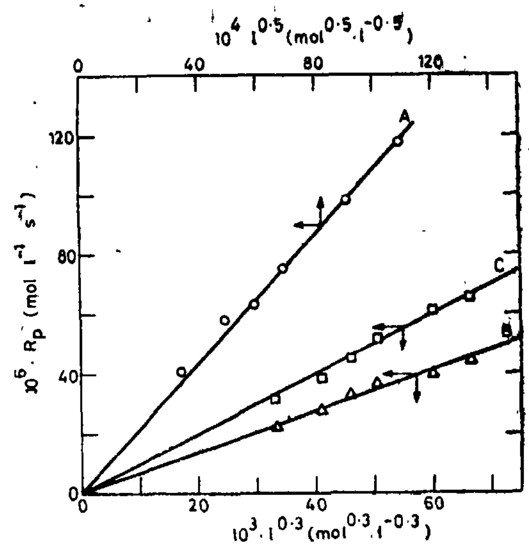


Fig. 3. Plot of rate of polymerisation versus initiator concentration at 45°C.

A. *Acrylamide*
[Aam] – 0.6308 M [$HClO_4$] = $8\times10^{-3} M$
B. *Methacrylamide*
[Mam] = 0.7014 M [$HClO_4$] = $8\times10^{-3} M$
C. *Methyl methacrylate*
[MMA] = 0.3705 M [$HClO_4$] = $8\times10^{-3} M$

The rate of polymerisation was studied over a range of concentration of the complex viz., $1.193\times10^{-5} M$ to $1.193\times10^{-4} M$. The rate of polymerisation was found to increase with increase of initiator concentration. The initiator exponent was found to be 0.5 in the case of acrylamide and 0.3 in the case of methacrylamide and methyl methacrylate (Fig. 3). The deviation from 0.5 order in initiator concentration for methacrylamide and methyl methacrylate polymerisation indicated that simultaneous termination by mutual combination and by complex molecule was taking place. Similar variations of the initiator exponent with different monomers have been reported by a number of workers. Venkatarao and Santappa[12] suggested termination by primary radicals in addition to the mutual combination to explain the deviation from half order dependence of the rate of polymerisation of methacrylamide photoinitiated by uranyl ions on the light intensity. Mitra *et al*[13] in their study of polymerisation of methyl methacrylate initiated by cuprous ion in acidic aqueous solution attributed the low initiator exponent, viz., 0.38, to the mixed termination, i.e., termination by mutual combination and by primary radicals. Steric factors[14] also had been advocated for such mixed terminations. If transfer reactions to the initiator were also taking place to an appreciable extent, the rate of polymerisation would be independent of initiator concentration (Eq. 7) which was not found to be the case.

The rate of polymerisation of the monomers increase with increase of temperature. A plot of the logarithmic rate of polymerisation against the reciprocal of the absolute temperature (Fig. 4) in the range 30°-50° gave 23.6 kJ mole^{-1}, 39.6 kJ mole^{-1} and 54.5 kJ mole^{-1} as the overall activation energy for acrylamide, methacrylamide and methyl methacrylate polymerisations respectively.

It was observed that polymerisation took place at $[H^+] = 4.2\times10^{-4} M$ while at $[H^+] < 4.2\times10^{-4} M$, there was no polymerisation at all. The rate of polymerisation was proportional to $[H^+]^{0.5}$ (Fig. 5).

Chainlengths :

On the basis of mutual termination, the kinetic chainlength which was a ratio of the rate of propagation and the rate of termination had been derived to be

$$n = \frac{k_p [M]^{\frac{1}{2}}}{(K\, k_i k_{t_1} . H^+ . C)^{\frac{1}{2}}}$$

The viscosities of the polymer samples prepared under various conditions of monomer concentration, complex concentration and acid concentration had been experimentally determined at 30±0.1°. A logarithmic plot of the chainlengths versus monomer concentration and complex concentration

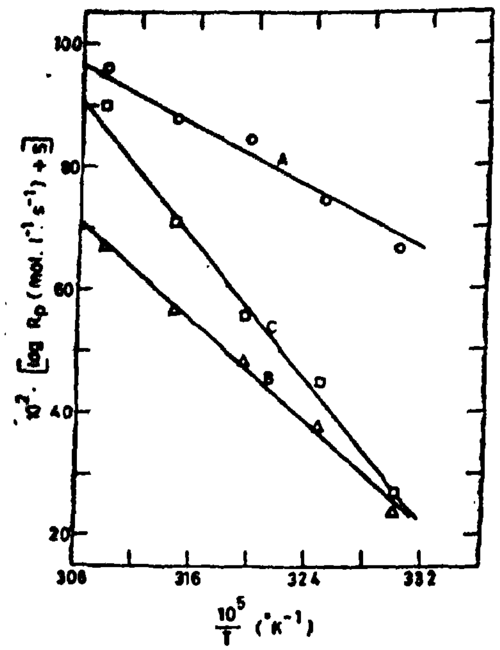


Fig. 4. Plot of rate of polymerisation versus temperature

A. *Acrylamide*
[Aam] = 0.6303 *M*, [Complex] = 4.768 × 10^{-5} *M*, [$HClO_4$] = 8 × 10^{-3} *M*

B. *Methacrylamide*
[Mam] = 0.7014 *M*; [Complex] = 4.768 × 10^{-5} *M*, [$HClO_4$] = 8 × 10^{-3} *M*

C. *Methylmethacrylate*
[MMA] = 0.3705 *M*, [Complex] = 4.768 × 10^{-5} *M*, [$HClO_4$] = 8 × 10^{-3} *M*

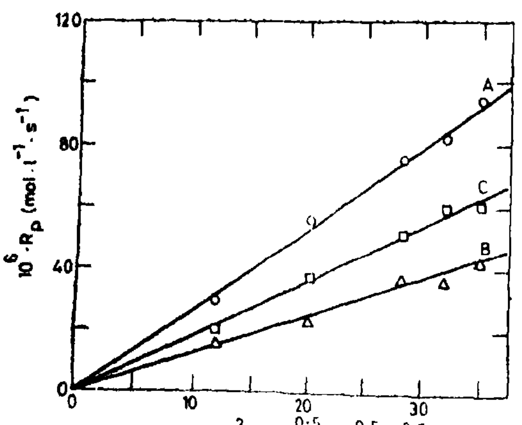


Fig. 5. Plot of rate of polymerisation versus hydrogen ion concentration at 45°C.

A. *Acrylamide*
[Aam] = 0.6303 *M* [Complex] = 4.768 × 10^{-5} *M*

B. *Methacrylamide*
[Mam] = 0.7014 *M* [Complex] = 4.768 × 10^{-5} *M*

C. *Methyl methacrylate*
[MMA] = 0.3705 *M* [Complex] = 4.768 × 10^{-5} *M*

had revealed the slopes to be 0.5 and −0.5 respectively (Fig. 6). Thus an additional confirmation for the kinetic scheme involving mutual combination had been obtained in addition to the direct evidence of the plots of the rates of polymerisation versus monomer concentration, complex concentration and the acid concentration. Thus all the kinetic data had been analysed by established procedures and equations for proving the mutual combination reactions.

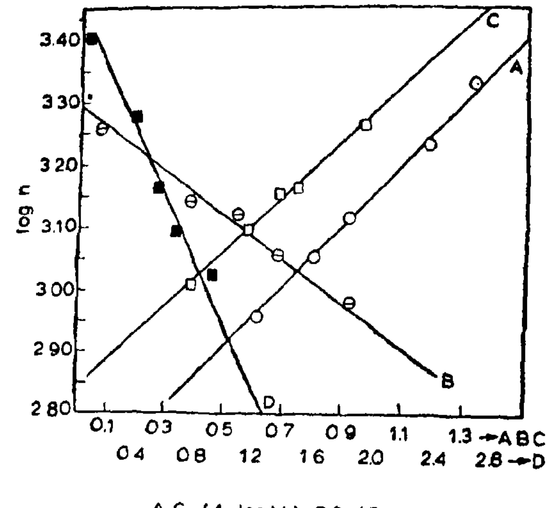


Fig. 6. Plot of chainlengths of polyacrylamide and poly(methyl methacrylate) versus monomer concentration and initiator concentration.

Polyacrylamide
A, Plot of log n versus (1+log M)
B; Plot of log n versus (5+log I)

Poly(methyl methacrylate)
C, Plot of log n versus (1+log M)
D, Plot of log n versus (5+log I)

It will be worthwhile pointing to the unique nature of this iron complex as an initiator of vinyl polymerisation. The conditions of acidity are very crucial in this study. Polymerisation does *not* proceed below hydrogen ion concentrations of 4.2 × 10^{-4} *M*. Such a requirement has not been reported previously. In the photopolymerisation of acrylamide by potassium *tris* oxalato ferrate(III), the rate was observed to increase with perchloric acid concentration along with the molecular weight[4]. The kinetic dependence was not reported. In the present work, with increasing polymerisation rates, the molecular weights decreased. Diethyl (dipyridyl) iron(III) functioned as an efficient initiator for the polymerisation of acrylonitrile[8]. 40% conversion was reported in 5 minutes and no kinetic parameters were reported, though the authors stated that the initiator exponent was not 0.5. A co-ordinated anionic mechanism was proposed from spectroscopic evidence. Ferric dipivaloylmethide initiated polymerisation of styrene

and methylmethacrylate, exhibited a monomer exponent of 1.5 and an initiator exponent of 0.5 just similar to the present investigation[15]. Initiation was proposed as due to the complex formed between the catalyst and the monomer, whereas in the present study, the decomposition of the iron complex proceeds independently of the monomer. The activation energy for the polymerisation of methylmethacrylate by ferric dipivaloylmethide complex was 27.2 K.cal.mole^{-1} in comparison with the activation energy of 13.1 K.cal.mole^{-1} for the initiator presently investigated.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 898-900

Electrochemical Reduction of Tellurite Ion at DME in Aqueous-Organic Solvent Mixtures

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Manuscript received 18 March 1978, accepted 9 July 1980

The present investigation deals with the polarographic reduction of tellurite ion (TeO_3^{2-}) in aqueous, aqueous-methanol, aqueous-ethanol and aqueous-dioxan mixtures. The reduction has been found to be diffusion controlled as verified by id vs $\sqrt{h}$ and Id vs C (concentration of TeO_3^{2-} ion) plots, which were linear and passing through origin in all cases. The plots of log (i/id-i) vs $E_{d.e.}$ (vs. S.C.E.) were linear in all the systems, but the values of slopes were much higher than required for six electron reduction (10 mV). These observations indicate the irreversible nature of electrode reduction. The kinetics of electrode process has been studied using Gellings' method and modified Koutecky's treatment. The values of kinetic parameters have been determined (K_s, $K^{\circ}_{f,h}$, and α_n). These values further confirm irreversible nature of reduction of TeO_3^{2-} ion. The nature of reduction has considerably been effected by changing the solvent composition There is no significant change in αn values with addition of organic solvent, so it is probably that there is no change in the mechanism of the electrode process. The analytical importance of the results obtained have been discussed.

POLAROGRAPHY has been widely used for the reduction of cations in different solvents[1-6]. However, the studies with the reduction of anions are only a few. The reduction of chromate, tellurate and iodate have been studied by Sadek *et al*[7] in aqueous alkanol mixtures and aqueous-dioxan mixtures. The reduction of chromate, bromate and iodate has been studied in detail in our laboratory by Gaur *et al*[8-9]. Lingane *et al*[10] studied the reduction of Te(IV) using ammoniacal buffer solutions. The reduction of Te(IV) in alkaline medium has been studied by Jamieson *et al*[11]. These authors indicated six electron reduction process and have discussed mechanism of the process.

Present paper deals with the polarographic reduction of TeO_3^{2-} in aqueous, aqueous-methanol, aqueous-ethanol and aqueous-dioxan media. The nature of electrode process being irreversible, the kinetic parameters have been calculated using Gellings'[12] theoretical treatment and modified Koutecky's[13] method.

Experimental

Stock solutions of tellurite ions (M/40), sodium hydroxide (1.0 *M*) and 0.2% gelatin were prepared by dissolving the required weight of reagent grade Na_2TeO_3, NaOH and gelatin in doubly distilled water. Solutions containing 0.5 mM tellurite ions, 0.1 *M* sodium hydroxide, 0.008% gelatin and required volume of organic solvent were taken. The current voltage curves were obtained by a manual set up. The DME having m 3.025 mg/sec and t = 2.7 sec (at 55 cm of mercury pressure) in 0.1 *M* NaOH with applied potential of 1.0 V (vs. S.C.E.) was used during all the measurements. The experiments were performed at 25±0.1° which was maintained with a Haake type ultrathermostat. The solutions were freed from dissolved oxygen by bubbling purified N_2 gas for 20 minutes. Methanol, ethanol and dioxan were purified using methods suggested by Bard[14].

Results and Discussion

The reduction was found to be diffusion controlled in each system which was confirmed by plotting the graph between i_d vs h and i_d vs C (conc. of tellurite ions). These plots were linear and pass through origin. The plots of log (i/id-i) vs $E_{d.e.}$ (S.C.E.) were linear in all cases and the slope values were higher than required for six electron reversible reduction (10 mV). This indicated the irreversible nature of electrode process. Hence reversible half wave potentials ($E^r_{\frac{1}{2}}$) has been calculated by using Gellings' treatment (Table 1). The values of kinetic parameters (standard rate constant Ks and transfer coefficient α) have also been evaluated by Gellings' method. Forward rate constant $K^{\circ}_{f,h}$ and transfer coefficient have also been calculated by Koutecky's method as extended by Gaur and Bhargava[15] (summarised in Table 2). The trend of variation of the values of transfer coefficient (α) by both the methods are nearly the same.

TABLE 1—SOLVENT EFFECT ON POLAROGRAPHIC CHARACTERISTICS OF TELLURITE WAVE IN 0.1 *M* NaOH

Sl. No.	Solvent	Percentage (by volume)	id(μA)	$-E_{\frac{1}{2}}$(V vs S.C.E.)	Slope (mV)	$D^{\frac{1}{2}} \times 10^{3}$ cm^2/sec	$-E^{r}_{\frac{1}{2}}$ (in volts)
1.	Methanol	10.0	12.15	1.2270	58	1.3886	1.2070
		20.0	10.80	1.2240	62	1.2028	1.1910
		30.0	10.08	1.2145	82	1.1226	1.1640
		40.0	9.63	1.2105	128	1.0780	1.1450
		50.0	9.45	1.2046	138	1.0624	1.1290
2.	Ethanol	10.0	11.88	1.2185	58	1.3265	1.1920
		20.0	9.99	1.2245	60	1.1154	1.1980
		30.0	9.36	1.2450	62	1.0487	1.2100
		40.0	8.91	1.2595	65.5	0.9982	1.2280
		50.0	8.19	1.2720	66	0.9184	1.2330
3.	Dioxan	10.0	10.98	1.2400	48	1.2218	1.2185
		20.0	10.71	1.2680	55	1.1999	1.2315
		30.0	10.26	1.2740	44	1.1505	1.2435
		40.0	8.82	1.2910	48	0.9890	1.2585
		50.0	8.19	1.3100	52	0.9199	1.2850
4.	Water	—	12.51	1.2200	35	1.3921	1.2000

TABLE 2—SOLVENT EFFECT ON KINETIC PARAMETERS OF TELLURITE ION IN 0.1 *M* NaOH

Sl. No.	Solvent	Percentage (by volume)	Gellings Treatment		Modified Koutecky's Method	
			αn	$K^{\circ}_{s} \times 10^{4}$ cm sec^{-1}	αn	K°_{fh} cm sec^{-1}
1.	Methanol	10.0	1.35	3.554	0.98	4.230×10^{-24}
		20.0	1.20	2.084	0.91	8.478×10^{-22}
		30.0	0.9	1.972	0.69	4.375×10^{-18}
		40.0	0.6	1.078	0.44	5.986×10^{-13}
		50.0	0.6	1.062	0.41	2.999×10^{-19}
2.	Ethanol	10.0	1.20	2.911	1.07	7.066×10^{-26}
		20.0	1.20	2.452	0.94	2.529×10^{-23}
		30.0	0.90	2.240	0.91	3.543×10^{-22}
		40.0	0.90	2.211	0.86	2.222×10^{-22}
		50.0	0.90	2.043	0.86	1.862×10^{-22}
3.	Dioxan	10.0	1.20	3.964	1.18	1.182×10^{-29}
		20.0	0.90	2.568	1.08	5.587×10^{-26}
		30.0	1.35	2.276	1.29	1.135×10^{-21}
		40.0	1.20	1.961	1.18	9.322×10^{-20}
		50.0	1.05	1.454	1.09	3.789×10^{-28}
4	Water	—	1.65	2.855	1.62	2.812×10^{-27}

It is a general observation that diffusion current decreases as the percentage of solvent increases from 10% to 50% (by volume). This change in diffusion current is due to viscosity effect by applying Ilkovic-Stoke relation, $id\eta^{\frac{1}{2}}$ = constant. The apparent decrease at higher proportions of the organic solvent can be ascribed to solvation of ions by the bulky organic molecules and the decreased solubility of the reducible salts.

The values of $E_{\frac{1}{2}}$ and $E^{r}_{\frac{1}{2}}$ have been found to shift in more cathodic direction as the percentage of ethanol and dioxan increases. However, the reverse trend is observed in case of methanol solvent. The shift in $E_{\frac{1}{2}}$ value with solvent has been discussed by Sadek *et al*[7] but no unified theory has been given so far. For reversible systems the difference in half wave potentials ($\Delta E_{\frac{1}{2}}$) due to transfer of the depolarizer from solvent 1 to solvent 2, as derived by Takahashi[6] using Born equation given as :

$$\Delta E_{\frac{1}{2}} = (E_{\frac{1}{2}})_2 - (E_{\frac{1}{2}})_1 = \frac{Ze}{Zr}\left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1}\right) \quad \dots (1)$$

But for irreversible system introducing standard electrode potential

$$(E_{\frac{1}{2}})_2 - (E_{\frac{1}{2}})_1 = \frac{Ze}{2}\,\frac{(\epsilon_2 - 1)}{\epsilon_2 r_2} - \frac{(\epsilon_1 - 1)}{\epsilon_1 r_1} + \frac{0.059}{na}$$

$$\log \left(\frac{1.349Kst^{\frac{1}{2}}}{Do^{\frac{1}{2}}}\right)_2 - \log \left(\frac{1.349Kst^{\frac{1}{2}}}{Do^{\frac{1}{2}}}\right)_1 \quad \dots (2)$$

Equation (2) indicates that the shift in the $E_{\frac{1}{2}}$ of an irreversible electrode reaction during the transfer

from one solvent to another is governed not only by the dielectric constant, but also by the change in the effective radius of the ion, and the kinetic parameters of the reaction. Accordingly, it is not easy to predict the magnitude of the $E_{1/2}$ shift of an irreversible process caused by changing the solvent. Irregular behaviour may also be due to the change of liquid, liquid junction potential, chemical nature of the solvent and ion-pair formation.

It has been observed that there is no significant change in the value of α_n with addition of organic solvent ; so it is probable that there is no change in the mechanism of the electrode reaction suggested by Lingane *et al*[10] i.e., six electron reduction in very alkaline solutions

$$TeO_3^{=} + 3H_2O + 6e^- \rightleftharpoons Te^{-2} + 6OH^-$$

The structure of double layer also plays an important role in the reduction of anions. The specific adsorption of anions at more cathodic potentials, the existence of the bulky organic molecule in the double layer, and the partial destruction of the aquo-layer surrounding the reducible ion, or its replacement by organic molecules make the reduction more difficult[15]. Hence the addition of organic solvent increases the irreversibility of the reduction which is obvious from Table 2.

The results are of analytical importance since tellurite ions can be estimated polarographically in the presence of organic solvents (methanol, ethanol and dioxan). Similarly tellurite ions can also be estimated in presence of other anions like arsenate, arsenite, molybdate, vanadate, selenate, etc. Tellurite can be estimated in trace quantity in 0.1 *M* NaOH in presence of these ions.

Acknowledgement

Authors are thankful to the University Grants Commission, New Delhi for providing Junior Research Fellowship to one of them (SKS).

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 901-903

Physico-Chemical Study of Vivianite

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Manuscript received 16 June 1979, revised 19 November 1979, accepted 9 July 1980

The present paper embodies a critical discussion about the structure of a phosphatic mineral, vivianite, with particular reference of the state of aggregation of its iron ion. The magnetic moment, electronic and infrared spectral studies have been reported. All these findings have been discussed from the point of view of its structure.

THE vivianite is a phosphatic mineral of iron having the chemical formula as $Fe_3(PO_4)_2.8H_2O$. It occurs as a sort of clay like blue pigments of fine crystalline aggregates distributed in diverse places in nature like the coal seams, bog-iron ore, etc. Further the formation of vivianite on ancient buried iron objects in peaty soil[1] and in association with the devitrified products of antique glasses buried in a humus-rich soil[2] is also reported in the literature. The origin of its blue colouration has been attributed to the oxidation of ferrous to ferric iron. The object of the present work is to furnish some crystallo-chemical information to that end.

The crystal structure of vivianite was determined by Mori and Ito[3]. It belongs to a monoclinic crystal class with the following crystallographic details :

$a_0 = 10.08$ Å, $b = 13.43$ Å, $c = 4.70$ Å, $\beta = 104°.30'$

with 2 molecules per unit cell.

The structure is built up of single and double octahedral groups of oxygen and H_2O around Fe ; and the phosphorus atoms are tetrahedrally surrounded by oxygen atoms. For the exhaustive details of its structural characteristics, the original paper of Mori and Ito[3] can be referred to. Some interesting accounts of its thermal characteristics are also reported in the literature[4-6]. It has a strong endothermic peak at 250°, followed by an exothermic peak at 650°.

Experimental

The mineral under investigation was collected as a discrete entity in coal fissures from a coal seam (Purushottampur) of Ranigunj coal field area. It was obtained in sufficient quantity for the present experimental purposes. It was also distributed as blue spots scattered over the surfaces of numerous coal chunks. Its composition was closely approximating to that of vivianite, $Fe_3(PO_4)_2.8H_2O$.

The X-ray powder diffraction pattern of the material, finely ground, was obtained in a cylindrical camera of radius 114.6 mm using FeKα ($\lambda = 1.9373$Å) radiation.

Magnetic measurement of the specimen was made by a sensitive Curie-balance at different temperatures ranging from 304.2°K to 90.0°K.

The electronic spectra of the compound $Fe_3(PO_4)_2.8H_2O$ were recorded (Fig. 2a and 2b) on a Beckman DB Spectrophotometer.

The infrared spectra of the compound were recorded on Beckman IR-20 model spectrophotometer using KBr pellet.

Results and Discussion

The identification of the crystalline phases was made by the usual method of Hanawalt *et al*[7]. The 'd' values of vivianite, $Fe_3(PO_4)_2.8H_2O$ (vide A. S. T. M., Card Index, No. 3-0070) with the

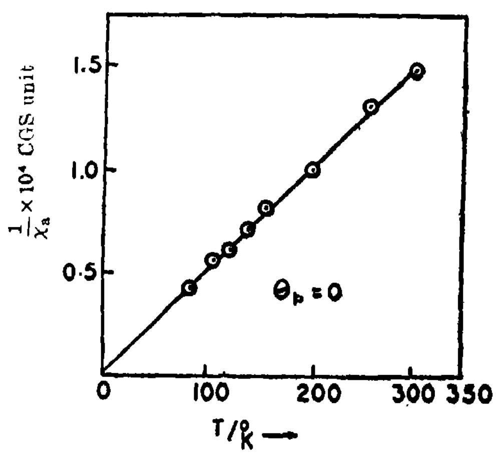


Fig. 1. $\frac{1}{\chi_a}$ against T/°K

* For correspondence : 2A, Lansdowne Lane, Calcutta-700 026.

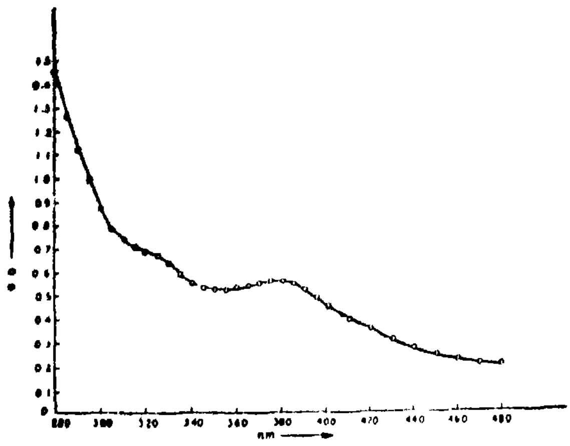


Fig. 2a—The electronic spectra of the vivianite.

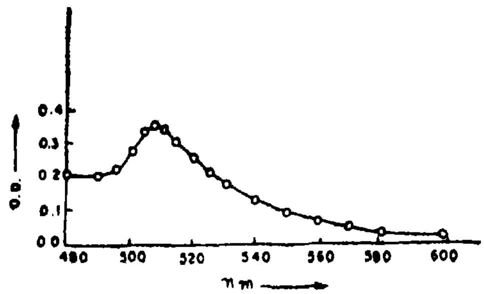


Fig. 2b—The electronic spectra of the vivianite.

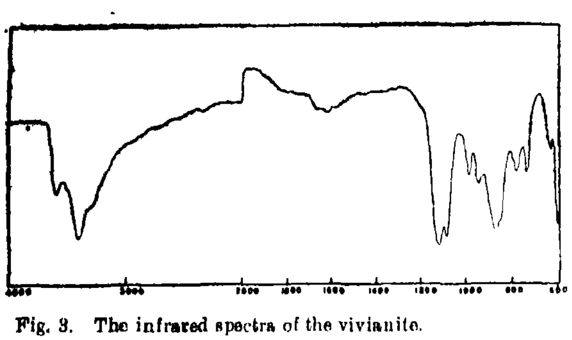


Fig. 3. The infrared spectra of the vivianite.

spacing of first three strong lines are 6.80Å (100), 2.97Å (67) and 2.71Å (67), with the relative intensity shown in the parenthesis. The evidence of the presence of any other phase was not found.

To obtain an insight into the colour problem of vivianite in relation to the valency state of iron, the usual magnetic method of analysis was extended to the above problem. The nature of bondings of iron ion with its surrounding ions, its coordination number, valency, etc., have a direct influence on the magnetic property of the element. The substance is found to be paramagnetic with the mass susceptibility value of 67.05×10^{-6} C.G.S. units at 304.2°K. Taking into consideration the molecular formula of the substance as $Fe_3(PO_4)_2.8H_2O$ and making diamagnetic correction, the mass susceptibility K_{Fe} (for single ion) comes to 11294×10^{-6} C.G.S. units at 304.2°K. The moment value of iron is found to be 5.28 Bohr/magneton.

It would be interesting to compare this value with the theoretical moment value of ferrous and ferric ions. The ferrous ions have a theoretical spin only moment value of 4.90 Bohr magneton, while ferric ions, with one more unpaired electron, have a moment value of 5.92 Bohr magneton. Again the variation of the square of the effective moment value (P^2_{eff}) of iron in experimental specimen from room temperature to 90°K is shown in the Table 1.

TABLE 1 MAGNETIC SUSCEPTIBILITY DATA

Experimental Specimen				Typical Ferrous salt $FeSO_4(NH_4)SO_4\ 6H_2O$ after Bose[16]	
Temp. (°K)	$\chi_a \times 10^6$ CGS unit	$\chi_m \times 10^6$ corr. CGS unit	P^2_{eff}	Temp. (°K)	P^2_{eff}
304.2	67.05	33885.6	27.74	296.8	28.49
262.1	77.07	38910.8	28.10	182.5	28.57
204.0	100.44	50637.3	27.75	84.8	27.13
106.7	123.975	62444.9	26.96		
142.3	139.85	70407.4	26.72		
123.5	160.728	80885.1	26.83		
109.1	181.48	91299.4	26.76		
90.0	219.55	110400.3	26.69		

Diamagnetic corr. $= 243 \times 10^{-6}$ CGS unit.

A plot of $\frac{1}{\chi_a}$ against T/K° (Fig. 1) is linear with zero θ_p value, indicating P^2_{eff} is independent of temperature.

The variation of $P^2_{eff} - T$ value of the experimental specimen is similar to that of the ionic ferrous salt (Table 1) and its variation of P^2_{eff} with temperature is small. As such the origin of its blue colour due to oxidation of ferrous to ferric iron (which is believed by some workers) is not evident from the present experimental results because iron exists in ferrous state in the mineral concerned.

The electronic spectra of the compound show absorption bands at 325 nm, 380 nm and 508 nm which is analogous to the absorption spectra of Fe^{2+} in a weak field of octahedral symmetry reported earlier[8-10]. Low and Weger[11], deduced the complete matrices for the energy level splitting of d^6 configuration (^5D ground state) in weak octahedral field. The first transition band ($^5T_{2g} \rightarrow {}^5E_g$) which is reported at about 10000 cm^{-1} in case of aquo iron(II) complex is found to be absent in the present compound. The observed

spectra show marked departure from reported one[11]. So the splitting of the electronic absorption bands in this may be attributed entirely to the splitting of excited state in this distorted ligand field.

The i.r. spectra of the $Fe_3(PO_4)_2.8H_2O$ with tentative assignment of the absorption bands has been compared with the spectra of ortho phosphoric acid[12]. The spectra (Fig. 3) show two strong bands at 1120 and 1090 cm^{-1}, which are attributed to the ionic phosphate vibration (P – O vibration)[13-15]. The bands in similar position (1150-1000 cm^{-1}) are reported in case of tribasic derivatives of orthophosphoric acid. The difference in the nature of P – O absorption bands in the present compounds from ortho phosphoric acid is due to bonding between P – O group and Fe^{+2} ion. The absorption bands at 3410 cm^{-1} and 1640 cm^{-1} in the spectra of the compound, correspond to OH stretching and bending vibration of the water of crystallization. In addition to above bands, a very sharp medium strong band at 3600 cm^{-1} due to presence of free OH stretching, has appeared. The sharpness of water absorption bands at 3410 cm^{-1} and 3600 cm^{-1} and high value of their OH stretching frequency (>3500 cm^{-1}) indicate that apparently there is very little hydrogen bonding in the compound.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 904-908

Mesomorphic Behaviour of Some Esters : Ethyl p-(p'-n-Alkoxycinnamoyloxy)Benzoates

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Manuscript received 1 February 1980, accepted 9 July 1980

A new homologous series of mesogenic esters ethyl p-(p'-n-alkoxycinnamoyloxy)-benzoates has been synthesized by treating trans-p-n-alkoxycinnamoyl chlorides with ethyl p-hydroxybenzoate and the phase transitions of the various ester mesogens have been determined. Monotropic nematic mesophase is exhibited alternately by the odd members up to the third derivative while the second member exhibits enantiotropic nematic mesophase. The second and third members show smectic mesophase in monotropic conditions. From the fourth member onwards enantiotropic mesomorphism is exhibited. Polymesomorphism begins from the second member though in the monotropic conditions. The nematic-isotropic (even) and smectic-isotropic transition curves, taken in continuation, show a gradual fall followed by a plateau and ending with another smooth fall ; the smectic-nematic transition curve shows a steep rise upto the hexyl member. From heptyl to octadecyl derivatives, only smectic mesophase is exhibited with definite transitions to isotropic liquid. While all the nematic phases are with threaded texture, the smectic mesophase shows focal conic Grandjean plates with fan shape texture. The usual odd-even effect is observed not only with regard to nematic mesophase but also the smectic mesophase which is a rare behaviour Similarities and contrasts with other homologous series yield interesting features. The thermal stabilities are comparable and the mesomorphic range as obtained is quite true to the molecular characteristics This homologous series of mesogens can be considered to be one of medium melting type though some characteristics of the high melting series are clearly exhibited. In all twelve new mesogens have been investigated for their characteristic behaviour.

LIQUID crystals belong to a class of compounds which are endowed with very specific characteristics of both liquids and crystalline bodies finding a co-existence over a range of temperature and or concentration. Besides academic interest in this specialized class of compounds, there has been sufficient interest aroused on account of their utility in various fields in recent times.

A search for newer and newer mesogens with low melting liquid crystalline properties has begun on a much wider scale due to their increased applications in the field of medicine and electronic display devices. Our present work incorporates synthesis of medium melting new mesogens and study of their characteristics.

Experimental

Synthesis and Study :

A. *Preparation of compounds :*

1. *p-n*-Alkoxybenzaldehydes : These are prepared by the method of Vyas and Shah[1].

2. Trans-*p-n*-alkoxycinnamic acids : These are prepared from the corresponding *p-n*-alkoxybenzaldehydes and malonic acid[2].

3. Ethyl *p*-hydroxybenzoates : *p*-Hydroxybenzoic acid (50 g) is added to absolute ethanol (200 ml) and concentrated sulphuric acid (2 ml). The mixture is refluxed on water bath for four hours and then poured on ice. The product so obtained is filtered, washed with aqueous sodium bicarbonate solution (4*N*) and water. It is crystallized from ethanol (95%) ; yield is 60%, m.p. 116°.

4. Trans-*p-n*-alkoxycinnamoyl chlorides : These are prepared from the corresponding acids[3].

5. Preparation of esters : Ethyl *p*-(*p'-n*-alkoxycinnamoyloxy)-benzoates are synthesized by treating trans-*p-n*-alkoxycinnamoyl chlorides with ethyl *p*-hydroxybenzoate. Dry ethyl *p*-hydroxybenzoate (0.01 mole) is dissolved in dry pyridine (A.R. 10 ml) and added slowly to the trans-*p-n*-alkoxycinnamoyl chloride (0.015 mole). The mixture is warmed while shaking for an hour and is allowed to stand overnight. It is acidified with cold dilute hydrochloric acid and the precipitates are collected by filtration and are washed with cold dilute sodium bicarbonate solution followed by water. The solid esters are crystallized from ethanol to fine needle-shaped crystals. Yield is approximately 60%. The elemental analysis is in conformity with the calculated values. The transition temperatures are given in Table 1.

TABLE 1—ETHYL *p*-(*p*'-*n*-ALKOXYCINNAMOYLOXY)-BENZOATES

n-Alkyl group	Transition temperature °C		
	Smectic	Nematic	Isotropic
Methyl	—	(101.0)	105.0
Ethyl	(83.0)	114.0	120.0
Propyl	(85.5)	(107 0)	122.0
Butyl	95.0	109.0	119.5
Pentyl	100 0	114.5	119.0
Hexyl	88.5	119.5	120.5
Heptyl	80.0	—	118.5
Octyl	89.0	—	121.5
Decyl	72.0	—	123.0
Dodecyl	75.0	—	120.0
Hexadecyl	87.0	—	116.0
Octadecyl	80.0	—	114.5

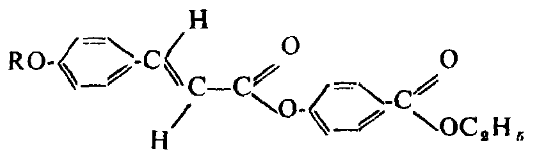
The values in the parenthesis indicate monotropy.

B. *Method of study :*

The transitions are studied by (i) the optical method as well as by (ii) using Kofler heating stage polarizing microscope.

Results and Discussion

The structure of the molecules of ethyl *p*-(*p*'-*n*-alkoxycinnamoyloxy)benzoates could be written down as follows :



The molecular structure which is more or less linear with two aromatic rings, one central bridge and sufficiently polar terminal groups at both ends, is quite conducive to exhibition of liquid crystallinity. The molecular geometry will suggest a degree of co-planarity giving almost an ideal length to breadth ratio. 'R' stands for alkyl groups whose chainlength will increase as one proceeds from CH_3 to $C_{18}H_{37}$.

The homologous series ethyl *p*-(*p*'-*n*-alkoxycinnamoyloxy)benzoates has lower transition temperatures than the corresponding trans-*p*-*n*-alkoxycinnamic acids[3] which also exhibit mesomorphism due to dimerization of molecules ; elimination of dimerization by formation of esters results into a series with lower transitions.

The various characteristic transitions of the homologues are plotted against the number of carbon atoms in the alkyl chain (Fig. 1). The first and third members are monotropic nematic mesogens while second member exhibits enantiotropic nematic mesophase. Both second and third members exhibit smectic mesophase in monotropic

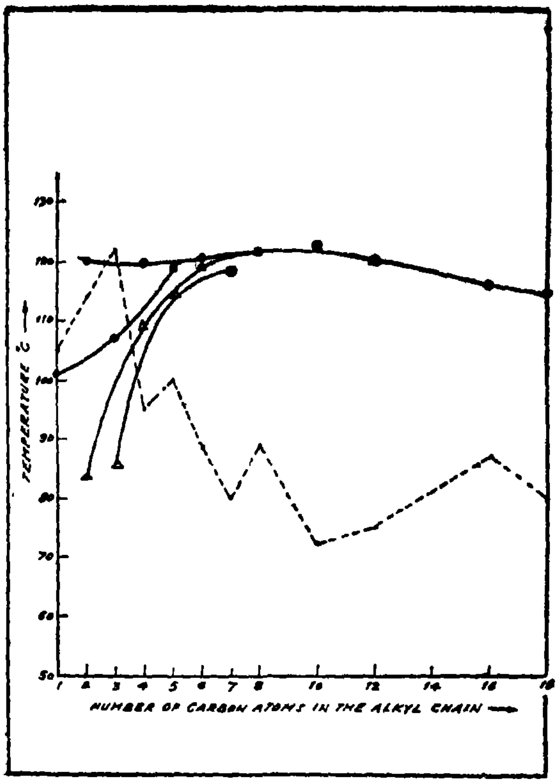


Fig. 1. Ethyl *p*-(*p*'-*n*-Alkoxycinnamoyloxy) Benzoates

------ Solid Mesomorphic or Solid Isotropic
△—△ Smectic-Nematic
○—○ Nematic-Isotropic
●—● Smectic-Isotropic

conditions. The solid-isotropic liquid or solid-mesomorphic curve is shown by dotted line : it rises up to the third member, after which it has a very steep fall up to the fourth member as the series is ascended. Thereafter a zig-zag nature of rise and fall is observed with an overall falling tendency up to the tenth derivative. This is followed by a gradual rise reaching a peak at the hexadecyl member and then a fall up to the end. On account of this the mesomorphic range narrows down and widens up alternatively. Polymesomorphism is exhibited from the fourth homologue since both smectic and nematic mesophases are shown by these members. From the seventh member up to the octadecyl derivative, only smectic mesophase is exhibited as the series is ascended.

There are two nematic-isotropic curves—one that connects the nematic-isotropic transitions having odd number of carbon atoms in the alkyl chain and the other that connects the even number of carbon atoms. The usual odd-even effect is observed, i.e. the nematic-isotropic transitions are alternating with odd and even number of carbon atoms in the alkyl chain. The reason as advanced[4]

is to be found in the molecular geometry and their orientation in the nematic liquid.

The nematic-isotropic transition temperature curve for the odd members of the alkyl chain show a rising tendency up to the pentyl derivative as the series is ascended. This tendency of rising transition curve has been considered to be a characteristic of low-melting mesogenic homologous series. The transition curve for the even carbon members shows a slight fall followed by an equally slight rise up to decyl homologue after which a smooth fall is observed as the series is ascended.

The two benzene rings contribute towards aromaticity and polarizability of the molecules. The central bridge again enhances the polarizability which increases with increasing length as well as the number of double bonds of the bridge ; these give rise to sufficient lateral attractions. The terminal groups with polar nature endow the molecules with terminal attractions which help maintaining an orientation of the molecules. Polar terminal attractions aided by the lateral forces orient the molecules in the fluid state which may be said to be the major factors in the exhibition of a mesophase.

It can be seen that, as far as the present series of mesogens is concerned, the polar nature of the terminal groups is sufficiently pronounced as compared to the forces arising out of the aspects of polarizability ; when end to end attractions are more pronounced, the nematic mesophase gets exhibited. When thermal energy is supplied to the molecules as temperature is raised, the molecules in the solid state are capable of resisting it preserving their domain structure intact, but only up to a limit after which, being incapable of resisting the vigorous thermal vibrations as set by the increasing supply of thermal energy, they break down to an isotropic fluid. However, in case of the mesogens, even after the molecules break down to a fluid condition, the terminal and lateral attractions due to the polar nature of the end groups as well as overall polarizability of the molecules, help holding the molecules in a parallel orientation in an end to end or layered manner before they pass into a random redistribution. This kind of parallel orientation of the molecules in the fluid state makes them to exhibit characteristic properties which are mesomorphic in nature. On further supply of energy, the thermal vibrations will increase ; a point will reach when the thermal vibrations overcome the resistance offered by the terminal and lateral attractions resulting into an isotropic liquid.

When the terminal attractions are more pronounced, the nematic mesophase will prevail. In this series the first three members show purely nematic mesophase though the second and third members exhibit smectic mesophase on super cooling. With increase of alkyl chain length as the series is ascended, the overall polarizability will be enhanced. The ratio of terminal attractions to lateral attractions decreases as the series is ascended ; the net result is that the lateral attractions gain a predominance over the terminal attractions. The molecules under such conditions will adhere strictly maintaining the layered structure, though partially they might acquire a fluid condition. Under such situation, the layered smectic structure is maintained giving rise to a smectic mesophase. As the temperature is further raised, the strict adherence of the molecules in the layered form gets weakened due to increased thermal vibrations. The molecules will slowly acquire more fluid nature, though they do not abruptly acquire any randomness. At a definite temperature, the layer structure breaks down, but end to end parallel orientation is still maintained giving rise to more fluidity and nematic threaded texture to the molecules. Thus polymesomorphism is exhibited from the second member up to the sixth members of the homologous series.

From the seventh members onwards, purely smectic mesophase is exhibited. The overall polarizability of the molecules gets enhanced as the chainlength of the alkyl chain at one end increases contributing to the exhibition of smectic texture. However, the ratio of terminal to lateral attractions is so low that at a certain stage the thermal vibrations break down the orientation of molecules without giving them a chance for adopting a nematic orientation. Thus only smectic mesophase prevails after the seventh member.

Polymesomorphism is exhibited from the second member up to the sixth homologue. The smectic-nematic transition curves show a steep rise ; there are two of them showing alternation effect. Usually an assumption is made that the alkyl chain adopts a zig-zag conformation[6] with the major axis of the chain statistically normal to the smectic planes. Thus each methylene unit will increase by the same amount the lateral intermolecular attractions on which smectic thermal stability predominantly depends. Therefore S – N temperatures should not alternate. However, the present homologous series deviates remarkably in this regard and while alternation in smectic-nematic transitions is not an usual phenomenon, the homologues of ethyl *p*-(*p*'-*n*-alkoxycinnamoyloxy)benzoates series exhibit alternation effect even for the smectic-nematic transitions, beginning from the second member up to the hexyl homologue. Though this behaviour is rare and remarkable, it has been observed earlier also in case of the homologous series of *n*-alkyl 4-*p*-methylbenzylideneamino- and 4-*p*-acetoxybenzylidene amino cinnamates[6]. Yet there is a vital difference between these two homologous series. In case of *n*-alkyl 4-*p*-acetoxybenzylideneaminocinnamates, the smectic-nematic transition

curves show a falling tendency while these in case of the present homologous series ethyl *p*-(*p*′-*n*-alkoxycinnamoyloxy)benzoates show a steep rising tendency.

A comparative statement of their thermal stabilities is given in Table 2; it can be seen that the smectic-nematic thermal stability for the present

TABLE 2 RELATIVE SMECTIC-NEMATIC THERMAL STABILITIES

Average transition temperature °C	Ethyl *p*-(*p*′-*n*-alkoxycinnamoyloxy) benzoates	*n*-alkyl 4-*p*-acetoxybenzylideneaminocinnamates[6]
even $C_2 - C_8$	103.8	112.0
odd $C_3 - C_5$	100.0	109.5

homologous series is less than that of the homologous series *n*-alkyl 4-*p*-acetoxybenzylideneaminocinnamates. Obviously there are two benzene rings in both the series under comparison; the terminal and central groups too match each other in the overall polarizability and the ratio of lateral to terminal attractions. On these counts the smectic-nematic thermal stabilities for both the series should have been the same. However, since the non-coplanarity of the molecules due to the bumping of oxygen atoms into the non-bonded sides of the adjacent hydrogens of the aromatic ring in the case of the present series and bumping of the hydrogen atom of the central azomethine group of the *n*-alkyl 4-*p*-acetoxybenzylideneaminocinnamate series[7] differs; the non-coplanarity is less in the latter than the first. More non-coplanarity will decrease thermal stabilities; this is the case as far as the present ethyl *p*-(*p*′-*n*-alkoxycinnamoyloxy)-benzoates homologous series is concerned.

The smectic-nematic thermal stabilities for the corresponding odd and even homologues of both the series have been calculated; on comparison the difference of thermal stability between the odd and even homologues in both series is almost the same, i.e. 3.8 in the present series and 2.5 in the *n*-alkyl 4-*p*-acetoxybenzylideneaminocinnamates homologous series.

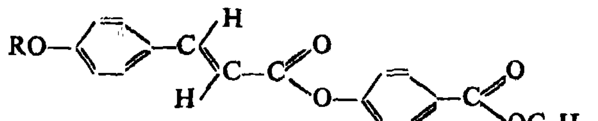
Thermal stabilities of the mesophases of this homologous series are compared with those of some similar homologous series studied earlier. Table 3 summarizes the thermal stabilities of the

TABLE 3—RELATIVE THERMAL STABILITIES

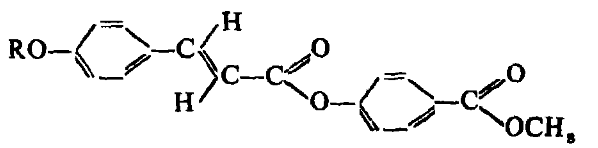
Average transition temperatures °C	Series A	Series B	Series C	Series D
Smectic-Nematic or	119.0 (C_8-C_{18})	133.7 (C_{12}-C_{18})	152.5 (C_7-C_{12})	148.8 (C_8-C_{10})
Smectic-Isotropic Nematic-Isotropic	119.7 (C_5-C_8)	138.25 (C_3-C_8)	163.0 (C_6-C_8)	205.0 (C_1-C_4)
Commencement of smectic phase	C_2	C_4	C_4	C_7

series under comparison. The molecules of the homologous series A differ from those of the homologous series B in that they have 'benzene ring $-CH_2-$Me' ester in

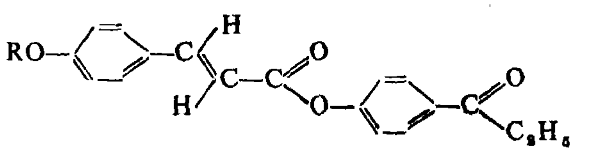
A. Ethyl *p*-(*p*′-*n*-alkoxycinnamoyloxy) benzoates



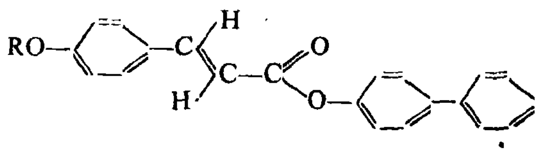
B. Methyl *p*-(*p*′-*n*-alkoxycinnamoyloxy)benzoates[8]



C. *p*-(*p*′-*n*-Alkoxycinnamoyloxy)propiophenones[9]



D. Biphenyl-4-trans-*p*-*n*-alkoxycinnamates[8]



place of 'benzene ring $-$Me' ester terminal group. Both smectic-nematic or smectic-isotropic and nematic-isotropic thermal stabilities get sufficiently decreased with the addition of $-CH_2$ group. As the terminal ester substituent ring $-CH_2-$Me is replaced by ring $-CH_2-CH_2-$Me group[10], both nematic and smectic thermal stabilities are further decreased. This progressive decrease in thermal stabilities of the mesophase has to be correlated with $-CH_2$ unit. The alkyl group is linked with the ester section through the O-linkage in case of the series A and B, the inductive effect due to additions of methylene, $-CH_2$, unit is rather less effective through O-linkage system than a direct linkage with C atom. Thus while increase in chain length increases polarizability thereby providing ground for enhancing thermal stability, the inductive effect as mentioned above results into weaker terminal attractions which cause progressive decrease in thermal stabilities with each methylene, $-CH_2$ unit added to the molecule.

The molecules of the homologous series C have the propionyl, $-COC_2H_5$ terminal group with ketonic bonding instead of the ester $-COOCH_3$ or $-COOC_2H_5$ terminal groups of the series B and A.

The thermal stabilities of the mesophases differ widely, those of the molecules with ring-ester groups being much lower. A comparison of the homologous series A and B with the homologous series D will show that while all other molecular features remain the same, the terminal ester $-COOC_2H_5$ or $-COOCH_3$ group is replaced by an aromatic ring in case of the molecules of the homologous series D. With a biphenyl ring, the overall polarizability increases besides a proportionate increase in the length of the molecules. Thus the thermal stabilities of the mesophases of the series D are very high as compared to those of the series A and B.

The early commencement of the smectic mesophase in the present series A can be attributed to the ester terminal groups; within the ester homologous series (A and B), the smectic mesophase commences earlier (at the second member) in case of series A than series B (at the fourth member) homologues which can be attributed to the increased chainlength of the series A molecules on account of additional $-CH_2$ unit which enchances overall polarizability of the molecules.

Acknowledgement

One of the authors (UAM) thanks the UGC for award of a Junior Research Fellowship during the tenure of which this investigation has been carried out.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 909-912

Investigations on the Behaviour of Potassium *n*-Butyl Xanthate and Benzamidothiosemicarbazide at D.ME.

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Manuscript received 31 March 1979, accepted 9 July 1980

Potassium *n*-butyl xanthate (PNBX) and benzamidothiosemicarbazide (BTSC) were studied at d.m.e. The polarographic studies carried out on the behaviour of PNBX and BTSC consist of the effect of concentration, *p*H, supporting electrolytes and mercury column heights. These waves were found to be diffusion controlled. In case of PNBX, $E_{1/2}$ (−0.22 volts) remained constant with the increase in *p*H, while in case of BTSC $E_{1/2}$ increased continuously with the increase in *p*H. Besides the studies on reversibility of the process, logarithmic analysis of the wave yielded straight lines with mean slope ratio of 0.033 volts (PNBX) and 0.032 volts (BTSC), showing reversible and two electron transfer process. The *p*K value (8.0) of BTSC has been evaluated from *p*H vs $-E_{1/2}$ plot The mechanism of the dimerisation of these compounds has been proposed.

THE polarographic behaviour of a number of sulphur compounds such as thiols, sulphydryl, cysteine, cystine, thiolactic acid[1,2] has been investigated in recent years. Compounds such as dithiocarbaminocarboxylic acid[3], thioglycolic acid[4,5], dithiocarbamate[6,7] and glutathione[8,9] showed anodic depolarization which was accompanied by salt formation, the general electrode process may be represented by the following equation

$$RSH + Hg \longrightarrow RSHg + H^+ + e$$

The electrode process is generally irreversible but in a few cases like the anodic depolarization of glutathione the reversibility of the process has been reported.

The electrode process does not merely depend on the nature and chemical composition of the adsorbate but is also highly dependent on the difference in crystalline orientation in the film of mercury salt. Thus it is clear that the conditions of forming adsorbate changes with the type of compound involved, e.g. cysteine showed the adsorption effect between *p*H 2-9, whereas glutathione gave a diffusion controlled wave directly proportional to concentration at least upto $2.0 \times 10^{-3} M$ in the whole *p*H range.

In floatation of sulphide minerals as xanthates the research workers and mill operators have long desired, a rapid method of xanthate determination, because most of the existing methods are long time consuming on account of the impurities which are invariably present in the floatation liquors. Therefore a detailed polarographic study of the behaviour of potassium *n*-butyl xanthate may prove useful in the feasibility of the polarographic method for its estimation in the presence of impurities. Another sulphur containing ligand benzamidothiosemicarbazide (BTSC) on account of its dual bonding sites nitrogen and sulphur showed potentiality as a good analytical reagent for metal estimation. Therefore, with a view to obtain information about the applicability of polarographic method in the study of metal-BTSC reaction, its behaviour has been studied at d.m.e. The information gathered during these studies are reported in this communication.

Materials and Methods :

Potassium *n*-butyl xanthate (hereafter designated as PNBX) and benzamidothiosemicarbazide (hereafter designated as BTSC) were synthesized and their purity was checked by chemical analysis. Fresh solution of PNBX in air free conductivity water and of BTSC in ethyl alcohol-water mixture was always used. All the other chemicals used viz. KCl, KNO_3, NaOH, $Na_2B_4O_7.10H_2O$, HCl, $HClO_4$, CH_3COONa, CH_3COOH etc. were of B.D.H. 'AR' grade and their solutions were prepared in doubly distilled water. Fresh solution of 0.2% gelatin used as maximum suppressor in these experiments, was prepared in warm water to avoid effect of ageing. Doubly distilled air free conductivity water was used in all the experiments.

A Toshniwal manual polarograph in conjunction with polyflex galvanometer (sensitivity 1 : 1, 1 : 10, 1 : 100) was used to record polarographic curves. The polarograph contained saturated calomel electrode connected to a cell through a salt bridge in conjunction with a d.m.e. having following characteristics, m = 1.942 mg/sec ; drop time t = 2.5 sec ; at the height of mercury column h = 40 cm. Triply distilled mercury was used for d.m.e. The inert

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atmosphere was maintained by passing purified nitrogen gas for about 15 minutes to ensure complete deaeration. *p*H metric measurements were carried out by Elico-*p*H meter model C_{10} India after allowing sufficient warming up period and standardizing with standard phthalate buffer (*p*H = 4) and borax buffer (*p*H = 9.2).

The following sets of the solution were prepared to study the polarographic behaviour of the PNBX and BTSC at d.m.e. In each set 2.0 ml of 2 *M* KCl and 2.0 ml of 0.2% gelatin were added before making required volume.

(i) *Effect of concentration of PNBX and BTSC in 0.16M KCl :*

1.0 ml, 2.0 ml, 3.0 ml, 4.0 ml, 5.0 ml each of 0.025*M* PNBX and BTSC were diluted to 25.0 ml with water (Table 1)

TABLE 1 VALUE OF i_d FOR PNBX AND BTSC AT VARIOUS CONCENTRATIONS IN 0.16 KCl

Concentration × 10^{-3} *M*	i_d(μA)		i_d/C	
	PNBX	BTSC	PNBX	BTSC
1.0	0.400	0.299	0.400	0.299
2.0	0.788	0.620	0.394	0.310
3.0	1.121	0.903	0.373	0.301
4.0	1.620	1.192	0.405	0.298
5.0	1.987	1.590	0.397	0.318

(ii) *Effect of concentration of PNBX and BTSC in 0.16M KNO_3 :*

1.0 ml, 2.0 ml, 3.0 ml, 4.0 ml, 5.0 ml, each of 0.025*M* PNBX and BTSC were diluted to 25.0 ml with water.

(iii) *Effect of pH :*

2.0 ml of 0.025 *M* PNBX solution was made upto 25.0 ml by the addition of suitable buffers of different *p*H ranging from 7.7 to 10.5 ; and 3.0 ml of 0.025 *M* BTSC solution was made upto 25.0 ml by the addition of suitable buffers of different *p*H ranging from 4.0 to 12.0. KCl and gelatin were added as usual before making the required volume (Table 2).

(iv) *Effect of heights of mercury column :*

1.0 ml each of 0.025 *M* of PNBX and BTSC was made upto 25.0 ml with water (Table 3).

TABLE 3—POLAROGRAPHIC DIFFUSION CURRENTS OF PNBX AND BTSC (1.0×10^{-3} *M*) AT VARIOUS HEIGHTS

Sl. No.	h_{eff} (cm)	$h_{eff}^{1/2}$	PNBX		BTSC	
			i_d(μA)	i_d/h_{eff}	i_d(μA)	i_d/h_{eff}
1.	30	5.48	0.310	0.010	0.299	0.009
2.	40	6.32	0.420	0.010	0.380	0.009
3.	50	7.07	0.520	0.010	0.453	0.009
4.	60	7.75	0.600	0.010	0.522	0.008

Results and Discussion

Current voltage curves of PNBX and BTSC gave current directly proportional to concentration ranging 1.0×10^{-3}*M* to 5.0×10^{-3}*M* and a linear relation was obtained between i_d and concentration of PNBX and BTSC (Table 1, Fig. 1).

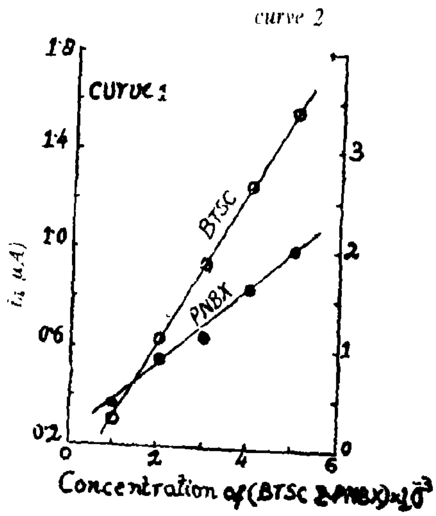


Fig. 1. Plot of i_d vs concentration.

TABLE 2—RESULTS FROM THE LOGARITHMIC ANALYSIS OF THE WAVES IN DIFFERENT BUFFERS (Fig. 2. Curves 1-6) and (Fig. 3. Curves 1-9)

Sl. No.	PNBX *p*H	PNBX i_d(μA)	PNBX $-E_{1/2}$(V)	PNBX Slope(V)	BTSC *p*H	BTSC i_d(μA)	BTSC $-E_{1/2}$(V)	BTSC Slope(V)
1.	7.7	2.110	0.22	0.036	4.0	0.901	0.123	0.028
2.	8.7	2.010	0.22	0.030	4.8	0.901	0.138	0.035
3.	9.0	1.850	0.22	0.034	5.5	0.891	0.160	0.029
4.	9.5	1.510	0.22	0.027	7.0	0.901	0.190	0.030
5.	10.0	1.282	0.22	0.031	8.0	0.901	0.220	0.035
6.	10.5	1.131	0.22	0.040	9.2	0.850	0.232	0.033
7.	—	—	—	—	10.5	0.860	0.240	0.035
8.	—	—	—	—	11.3	0.890	0.251	0.039
9.	—	—	—	—	12.0	0.890	0.260	0.032

The half-wave potential $E_{1/2} = -0.22$ volt (PNBX) and $E_{1/2} = -0.1$ volt (BTSC) of the waves at various concentrations remained constant. Approximately it can be taken as a criterion of reversibility of the wave.

Well defined anodic waves were obtained between *p*H 7.7-10.5 in case of PNBX (Fig. 2, Curves 1-6) and between *p*H 4.0 to 12.0 in case of BTSC (Fig. 3, Curves 1-9). All the plots of log $\frac{i_d - i}{i}$ vs $-E_{d.e.}$ yielded straight lines with mean slope ratio 0.033 V (PNBX) and 0.0326 V (BTSC), showing reversible and two electron transfer process (Table 2). From the data it is clear that the half wave potential remained constant in case of PNBX while it is shifted to more negative values with increasing *p*H in case of BTSC. In case of PNBX, i_d decreases with increasing *p*H, however i_d remained constant in case of BTSC.

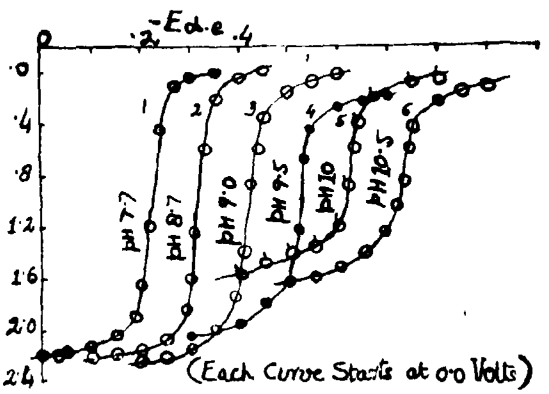


Fig 2. Effect of *p*H on Polarographic Behaviour of PNBX.

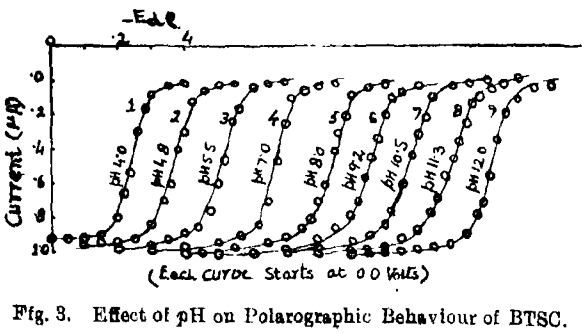


Fig. 3. Effect of *p*H on Polarographic Behaviour of BTSC.

In case of BTSC, the plot of $-E_{1/2}$ vs *p*H gave straight line upto *p*H 8.0 (Table 2. Fig. 4). The intersection of these lines gave the value of dissociation constant (pK_1) 8.0.

A series of polarograms of PNBX and BTSC, both at fixed concentration ($1.0 \times 10^{-3} M$) were

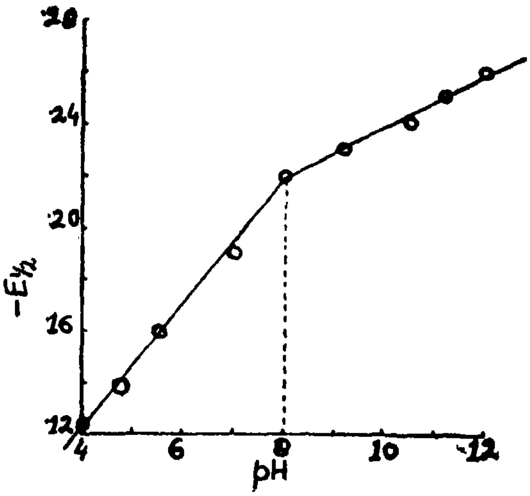


Fig. 4. Plot of *p*H vs $E_{1/2}$

recorded at different heights of mercury column. In both the cases, well defined anodic waves were obtained over the whole range. A linear plot of i_d vs $h_{eff}^{1/2}$ (Table 3, Fig. 5) showed that the reaction was diffusion controlled in both the cases.

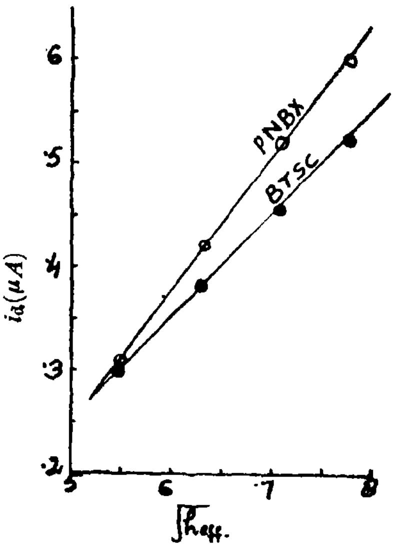
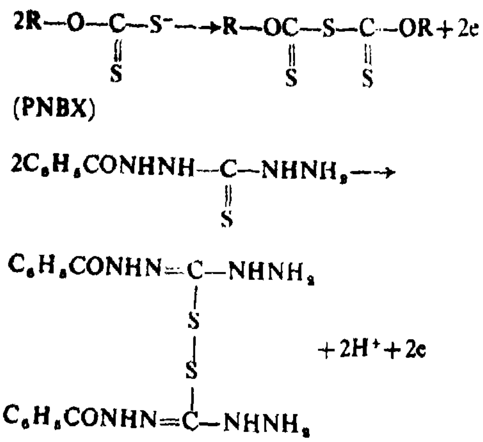


Fig. 5. Plot of i_d vs $\sqrt{h_{eff}}$

Usually sulphur containing organic compounds such as thioureas, cystein etc., gave anodic waves resulting in the formation of mercury sulphides and the reactions have been shown one electron transfer.

A mechanism involving dimerisation of PNBX and BTSC is proposed explaining the two electron

transfer reaction



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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 913-914

Synthesis of N¹-(β-cyanoethyl)-2-heterocyclic-(*p*-arylidene)-aminobenzenesulphonamides and Their Insecticidal Activity

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Manuscript received 7 May 1979, revised 25 February 1980, accepted 9 July 1980

Various substituted cyanoethylated sulphonamides were prepared and screened for their insecticidal activity. They showed excellent insecticidal activity on male and female cockroachces.

A large number of cyanoethylated sulphonamides are known to possess insecticidal activity[1-3]. Kretov *et al*[4] have reported the cyanoethylation of sulphanilamide and sulphapyridine. In continuation of our earlier interest in incorporating a cyanoethyl group in substituted sulphonamides[5], capable of exhibiting insecticidal activity, it was thought to synthesize N¹-(β-cyanoethyl)-2-heterocyclic-(*p*-arylidene)aminobenzenesulphonamides. Subsequently these sulphonamides were converted into amines and tetrazoles which exhibited antibacterial and anti-inflammatory activity[6,7]. The present communication describes the synthesis and insecticidal activity of N¹-(β-cyanoethyl)-2-heterocyclic-(*p*-arylidene)aminobenzenesulphonamides.

The i.r. spectra of the compounds showed absorption in the range of 2215 to 2260 cm⁻¹ due to $-C\equiv N$ stretching vibration. The respective asymmetric and symmetric stretching modes of vibration of S=O appeared in the range of 1330 to 1380 cm^{-1} and 1150 to 1180 cm^{-1}. The compounds also showed absorption band in the range of 1615 to 1640 cm^{-1} due to $>$C=N— stretching vibration.

Experimental

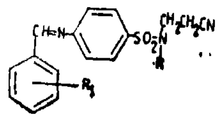
Melting points were taken in open capillary tubes and are uncorrected. The i.r. spectra were taken on Perkin-Elmer 137 and 177 spectrophotometers.

The Schiff's bases of N¹-2-heterocyclicsulphanilamides were prepared by the condensation of different substituted sulphanilamides with aryl aldehydes[8-10].

Synthesis of N¹-(β-cyanoethyl)-2-heterocyclic-(p-arylidene)aminobenzenesulphonamide [1-24] :

To a well stirred solution containing N¹-2-heterocyclic-(*p*-arylidene)aminobenzenesulphonamide (0.01 mole), pyridine (20 ml) and 'Triton B' (1 g) was added dropwise acrylonitrile (0.01 mole) at 30-35°. The mixture was stirred for 35 to 48 hours at room temperature. It was acidified and poured into ice water. The solid mass was obtained which was crystallized from alcohol. The results are cited in Table 1.

TABLE 1—N¹-(β-CYANOETHYL)-2-HETEROCYCLIC)-*p*-ARYLIDENE AMINOBENZENESULPHONAMIDES



Sl. No.	R₁	Yield %	m.p. °C	Mean K.D. time (hr)% concentration 0.5	0.1
	R=Pyrimidyl				
1.	H	60.00	220	8.0	10.5
2.	*p*-OH	75.00	210	7.0	9.5
3.	*o*-OH	70.00	235	6.5	8.0
4.	*p*-Cl	66.50	242	6.0	7.0
5.	*p*-$(CH_3)_2N$	58.00	200	7.0	8.5
6.	*p*-CH_3CONH	72.00	250	9.0	11.5
	R=4-Methyl pyrimidyl				
7.	H	75.00	150	7.0	10.5
8.	*p*-OH	75.00	228	6.5	9.0
9.	*o*-OH	73.00	242	7.0	8.5
10.	*p*-Cl	73.00	225	5.0	6.5
11.	*p*-$(CH_3)_2N$	77.00	230	7.5	10.0
12.	*p*-CH_3CONH	78.00	240	8.0	9.5
	R=4,6-Dimethyl pyrimidyl				
13.	H	66.66	195	8.0	11.5
14.	*p*-OH	70.20	243	7.5	10.5
15.	*o*-OH	61.50	265	6.5	10.0
16.	*p*-Cl	71.40	242	6.0	9.5
17.	*p*-$(CH_3)_2N$	74.00	180	9.0	12.0
18.	*p*-CH_3CONH	77.00	208	10.0	14.0
	R=Thiazolyl				
19.	H	72.00	220	9.5	12.0
20.	*p*-OH	72.70	150	8.5	10.5
21.	*o*-OH	69.20	168	7.5	10.0
22.	*p*-Cl	80.40	228	7.0	9.0
23.	*p*-$(CH_3)_2N$	70.00	265	9.0	14.0
24.	*p*-CH_3CONH	78.00	200	11.0	12.0
	Standard Insecticide Parathion			4	5.5
	Solvent Acetone			40	40

Insecticidal Activity : The compounds listed in Table 1 were screened for their insecticidal activity on male and female cockroaches by the method of Nash[11]. Acetone solutions of the compounds were applied at a dosage of 0.02 ml of .5% and .1% concentrations. Parathion, a standard insecticide, was used for control.

The data in table show that all compounds have insecticidal activity. Maximum insecticidal activity was observed in compound No. 10 and minimum in compound No. 18. It indicates that substitution of *p*-Cl group in arylidene moiety increased the insecticidal activity. A definite-structure activity relationship could not be established from the results obtained.

Acknowledgement

The authors wish to thank the Head of Chemistry Department, Lucknow University, Lucknow for providing laboratory facilities. One of them (R.R.) is indebted to I.C.M.R. for the award of a Junior Research Fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 915-917

Colour Reaction of Diphenylamine with Aldehydes

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Manuscript received 3 August 1979, revised 28 March 1980, accepted 9 July 1980

Diphenylamine reacts with aldehydes in acidic solutions. Diphenylamine salts (hydrochloride, sulphate and perchlorate) react with aldehydes directly. These reactions may be divided into two classes ; the first is based on formation of very stable ternary iminium salts, and the second class depends on the formation of highly unstable and deliquescent ternary iminium salts. Latter salts are autoxidized with atmospheric oxygen to give a deeply coloured compound which can be used for the sensitive colorimetric detection and determination The ternary iminium perchlorate obtained may be used as explosives.

DIPHENYLAMINE is an important analytical reagent. It has been used in many oxidation reduction titrations[1]. It has been used as a chromogenic reagent in the detection and determination of aldehydes[2,3,4], sugars[5,6] vanadium[7,8] etc. Qureshi *et al*[2] have published a sensitive and selective resin spot test for diphenylamine. For this test the limit of identification was found to be 0.25 μg in a limiting dilution of $1:2\times10^4$. The test is based upon the reaction of diphenylamine with *p*-dimethylaminobenzaldehyde in the presence of hydrochloric acid. In this reaction they have noted that a yellow colour is formed which on heating turns green or bluish green. The coloured products obtained from the reactions of diphenylamine with sugars have been studied by Mamose *et al*[5,6]. Recently[4] diphenylamine has been used as a general reagent for the spectrophotometric determination of aromatic aldehydes. Aromatic aldehydes and some of their binary mixtures can be determined. The maximum error was found to be $\pm$ 6 and $\pm$ 10% for single and for simultaneous determination of aldehydes respectively. However, the isolation and identification of diphenylamine-aldehydes reaction products have been found to be difficult and it has not been reported so far.

Now an attempt is made to isolate and identify the coloured products of these reactions. The results obtained are discussed below. Diphenylamine reacts with aldehydes in acidic solutions. Its salts (hydrochloride, sulphate and perchlorate) react with aldehydes directly. These reactions may be divided in two classes. The first is based on the formation of a very stable ternary iminium salt as it is found in the case of cinnamaldehyde and its derivatives. To 2.7 gm (0.01 mole) of diphenylamine perchlorate solution in ethanol (20 ml) in a conical flask was added 2.6 ml (0.02 mole) of 97% cinnamaldehyde. On swirling, crystals separated with the evolution of heat. The crystals were filtered, washed with ether and recrystallized from acetonitrile. The yield was high (90%). The product has m.p. 195°. The following structure may be proposed for this product, N-cinnamyldenediphenyliminium perchlorate.

$$\underset{C}{Ph}-\underset{B}{CH}=\underset{D}{CH}-\underset{A}{CH}=\overset{+}{N}\,\underset{C}{Ph_2}ClO_4^- \qquad \text{(R)}$$

The following are the evidences in support of the above structure. The presence of chlorine in compound(R) was found to be positive. An explosive cracking on heating (R) indicates the presence of perchlorate ion. The acidic solution of (R) hydrolysis on adding water in excess indicate the presence of $>C=\overset{+}{N}<$. The elemental analysis results are the following :

		C	H	N
Per cent	Found	65.40	4.69	3.74
	Calculated	65.70	4.70	3.60

I.R. analysis by KBr method shows the absence of $>NH$ and $>C=O$ bands and the presence of a new strong absorption band at 1660 cm^{-1} indicative of $>C=\overset{+}{N}<$. The N.M.R. spectra consisted of signals occurring at $\delta=9.1$ (J=10Hz, d,A), $\delta=8.26$ (J=15Hz, d,B), $\delta=7.50$ (s,C) and $\delta=7.03$ (J=10.74, q,D) in trifluoroacetic acid at 60MHz Varian. Signal at $\delta=7.50$ consists of a shoulder at $\delta=7.65$; it may be due to the fact that two of the phenyl groups are attached to $=\overset{+}{N}$. The assignments are made as shown in compound (R). N.M.R. data for ternary iminium salts have been discussed in detail by Leonard *et al*[9]. U.V. spectrum in methanol consists of a strong absorption band indicative of $>C=N<$ at 283 nm. E.P.R.

spectrum shows no signals. The X-ray data obtained (Table 1) show that this is a new compound. Similar compounds have been isolated and identified by *Leonard et al*[9]. Ternary iminium salts obtained in this class are very stable in air. Like other organic perchlorates they may be suitable for using as explosives[10]. They may also be used in synthetic chemistry because they are very prone to nucleophilic[9] attack.

TABLE 1—X-RAY DATA FOR N-CINNAMYLDENEDIPHENYLIMINIUM PERCHLORATE

d values	I/I_0	d values	I/I_0
12.989	9	2.882	8
9.817	14	2.794	11
9.017	30	2.761	12
7.019	13	2.696	6
6.804	13	2.619	12
6.320	14	2.493	5
6.032	19	2.372	7
5.467	10	2.330	5
4.951	12	2.231	6
4.766	40	2.102	6
4.571	53	2.013	5
4.480	43	1.458	95
4.267	48	1.451	23
4.111	35	1.414	15
4.037	39	1.403	15
3.863	36	1.392	86
3.767	51	1.383	95
3.705	32	1.362	100
3.559	20	1.353	99
3.424	16	1.323	95
3.299	16	1.320	74
2,252	12	1.317	95
3.076	14	1.310	60
2.976	15	1.304	20

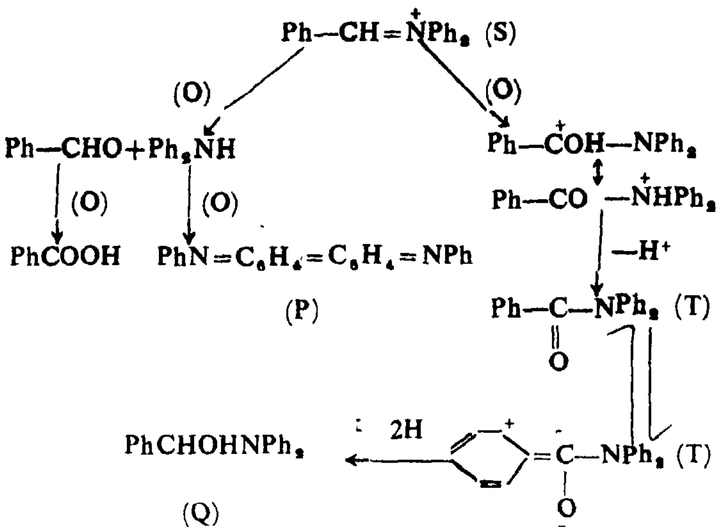
The second class of diphenylamine-aldehydes reactions depends on the formation of highly unstable and deliquescent ternary iminium salts (S). These salts may either autoxidise with atmospheric oxygen to give a deeply coloured compound(T) or decompose to give the reactants. The amine and the aldehyde so obtained may autoxidise to give a deeply coloured compound(P) and the corresponding acid via the peroxide free radical respectively. This type of ternary iminium salts are obtained from the reaction of diphenylamine with benzaldehyde O-vanilline, anisaldehyde and salicylaldehyde. To 5 ml (0.05 mole) of benzaldehyde in 250 ml of carbon-tetrachloride was added 4.2 gm (0.025 mole) of diphenylamine. A clear solution was obtained which gives a soft yellow precipitate on adding concentrated hydrochloric acid (0.5 ml) dropwise with continuous shaking. Perchloric acid or sulphuric acid can be used in place of hydrochloric acid. The precipitate so obtained was filtered, washed with carbon tetrachloride and dried at 25°. To 2 ml (0.02 mole) benzaldehyde in 10 ml ethanol was added 2.7 g (0.01 mole) diphenylamine perchlorate. A yellow solution was obtained which turns green on heating (100°) for half an hour. After cooling (0°) a green gummy precipitate was obtained. The precipitate so obtained was filtered, washed, dried at 30° and then dissolved in acetonitrile-perchloric acid (1 : 1) mixture. From this solution a green product was precipitated by adding water in excess. The product was filtered, washed with water and ethanol and dried.

TLC studies in methanol and chloroform showed that the yellow product consists of a green compound that turns bluish green in air (Rf value zero and diphenylamine hydrochloride (Rf value 1). The yellow product was dried at 25° for 2 hours and then its X-ray pattern was recorded. The product was found to be crystalline (Table 2, column 1). After 24 hours drying (25°) it turns partly green and partly pale yellow. It was found to be crystalline (Table 2, column 2). After 4 days drying at the same temperature it turns bluish green and found to be poorly crystalline (Table 2, column 3). The relative intensity of the X-ray lines for three phases have been given in Table 2.

TABLE 2—X-RAY DATA OF BENZALDEHYDE-DIPHENYLAMINE HYDROCHLORIC ACID PRODUCT

After 2 hours drying at 25°C		After 24 hours drying at 25°C		After 4 days drying at 25°C	
-	—	7.248	19.8	—	—
6.505	18.0	6.505	19.8	—	—
5.675	19.8	5 749	28 8	—	—
5.466	20.7	5 467	34.2	—	—
5.053	20 7	5.032	28.8	—	—
4.480	21.6	4.800	36.0	—	—
4.111	34.2	4.111	61.2	—	—
—	—	4.073	57.6	—	—
3.931	46.8	3.931	100.0	3.931	32.4
3.616	23.4	3.616	30.6	—	—
3.450	25 2	3.477	32.4	—	—
3 324	19.8	3.348	23.4	3.203	19.8
3.162	27.0	3.184	34.2	3.184	18.0
3.118	18 0	—	—	—	—
3.015	18 0	3.035	16.2	—	—
2 882	19.6	2.882	18.0	2 909	16.2
—	—	2.829	10 8	—	—
2 714	18.0	2.761	25.2	—	—
—	—	2.712	23.4	2.712	14.4
2.696	18.0	2.605	10 8	—	—
2.605	14.4	2.466	19.0	2.440	12.6
2.330	12.6	2.342	12.6	—	—
2.285	12.6	2.296	10.8	—	—
—	—	2.274	12.6	—	--
2.199	10.8	2.105	7.2	—	—

X-ray data recorded in table 2 are corresponding to diphenylamine hydrochloride (ASTM 5.0326). On the basis of these results it may be concluded that the yellow product is a mixture of non-crystalline ternary iminium salt (S) and crystalline diphenylamine hydrochloride. The yellow ternary iminium salt rapidly oxidizes to green compound (T) and diphenylamine hydrochloride slowly oxidizes to blue compound (P).



For green compound(T) I.R. spectrum by KBr method consists of a strong and broad band from 1637 to 1680 cm^{-1}. N.M.R. spectrum in deuterated dimethylsulphoxide and D_2O on 90 MHz Varian consists of a signal at $\delta = 8.94$ (J=20 Hz, t, 3 Ph). On treating green solution with zinc dust decolorization occurs. The elemental analysis results are the following for compound (T)

		C	H	N
Per cent	Found :	84.40	5.75	4.89
	Calculated :	83.50	5.40	5.10

The intense colour of the green product is consistent with the large conjugated system of zwitter ionic structure (T). This type of colour stuff has been studied by Acheson *et al*[11]. Streuli and Averell[12] have remarked, "the Schiff base produced by condensation of an amine with an aldehyde in strong acid solution, can be oxidized by atmospheric oxygen to give a coloured material". Similar opinion has also been given by Feigl[13].

The colour of the oxidized material is more intense than that of the ternary iminium salt. Thus, it can be used for the sensitive colorimetric detection and determination. The oxidation occurs at a very high rate in dimethylsulfoxide. Thus it seems to be a good analytical reagent.

Acknowledgement

The authors thank Prof. Asif-uz-Zaman for facilities and important discussions.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 918-919

Synthesis of Some New Mannich Bases of N-(4-Hydroxy-3-methoxy-benzylidene)-4-methoxy benzoic acid hydrazide as Potential Biologically Active Agents

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Manuscript received 23 March 1979, revised 25 September 1979, accepted 9 July 1980

A series of new Mannich bases from N-(4'-hydroxy-3'-methoxy-benzylidene)-4-methoxy benzoic acid hydrazide has been synthesised and evaluated for their antibacterial and antiviral activities.

A large number of the hydrazides and hydrazones have been tested as antibacterial, antiviral and antitubercular agents[1-8]. Besides, piperazine and other heterocyclic amino derivatives have been synthesised as biologically active agents[9-10]. In view of these observations, it was considered worthwhile to synthesise certain new Mannich bases from N-(4'-hydroxy-3'-methoxy-benzylidene)-4-methoxy benzoic acid hydrazide(I). I was prepared according to the reported method[11] from 4-methoxybenzoic acid hydrazide[12] and vanillin. I was then condensed with different secondary amines in the presence of formalin under Mannich conditions, to yield II, according to the scheme (1).

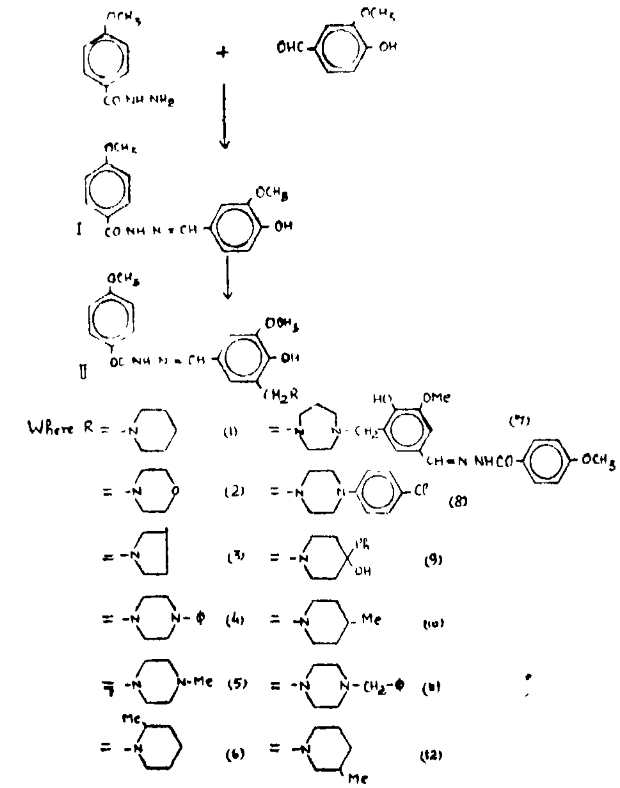
Mannich condensation with I could conceivably have given product with alternative structure IIa but interpretation of nmr spectrum of the compound No.6 based on the following results confirms that only structure II was formed :

3.20 τ (singlet, 1H), 3.19 τ(doublet, J = 9Hz, 2H), 2.87 τ (broad singlet, 1H), 1.97 τ (doublet, J = 9Hz, 2H), 1.57 τ (broad singlet, 1H), −0.50 τ (broad singlet, exchangeable with D_2O, 1H), −1.16 τ(hump, exchangeable with D_2O, 1H).

Presence of three protons as singlets in the aromatic region together with two exchangeable protons in nmr spectrum of compound 6 completely rules out possibility of structure IIa.

In case of compound 6 and 12 the stereochemistry of methyl group could not be definitely ascertained because of overlapping of nmr signals in the region 5.8-8.9 τ, it was difficult to analyse the splitting pattern of methine protons adjacent to the nitrogen of piperidine ring in the compound numbers 6 and 12.

All the synthesised compounds have adequately been characterised by correct elemental and infrared spectral studies.



Scheme 1

Experimental

Melting points were taken in open capillaries and are not corrected. Infrared spectra were recorded on a Perkin-Elmer 137 G Spectrophotometer in KBr.

N (4'-Hydroxy-3'-methoxy-benzylidene)-4-methoxy-benzoic acid hydrazide(I) :

4-Methoxybenzoic acid hydrazide (1 mole) and vanillin (1 mole) were refluxed in ethanol with 3

drops of glacial acetic acid for 4 hr. The product obtained on cooling, was filtered and recrystallised from ethanol (pale yellow needles) m.p. 203° (lit[9] 203-204°), yield 90%.

5-Substituted aminomethyl-N-(4'-hydroxy-3'-methoxy-benzylidene)-4-methoxybenzoic acid hydrazides(II) :

The hydrazone I (0.1 mole) was condensed with formaldehyde (0.15 mole) and secondary amine (0.1 mole) in ethanol by refluxing for 4 hr. Excess of the solvent was distilled off and product thus obtained was filtered and recrystallised from a suitable solvent. II, thus obtained are listed in Table 1.

TABLE 1—5-SUBSTITUTED AMINOMETHYL-N-(4'-HYDROXY-3'-METHOXY BENZYLIDENE)-4-METHOXY BENZOIC ACID HYDRAZIDES(II)

Compound No.	Molecular formula	m.p °C	% Nitrogen Calculated	Found
1.	$^{c}C_{22}H_{27}N_3O_4$	211-212	10.50	10.60
2.	$^{c}C_{21}H_{25}N_3O_5$	205	10.50	10.00
3.	$^{b}C_{22}H_{25}N_3O_5$	190-91	10.96	10.80
4.	$^{a}C_{27}H_{30}N_4O_4$	224-25	11.81	11.32
5.	$^{a}C_{22}H_{28}N_4O_5$	217-18	13.59	13.25
6.	$^{a}C_{23}H_{29}N_3O_4$	188-189	10.24	10.90
7.	$^{b}C_{20}H_{44}N_4O_5$	138-140	11.60	11.46
8.	$^{b}C_{27}H_{29}ClN_4O_4$	213-15	11.02	10.82
9.	$^{b}C_{27}H_{31}N_3O_5$	233-34	8.80	8.59
+10.	$^{d}C_{23}H_{29}N_3O_4$	208		
*11.	$^{d}C_{23}H_{29}N_4O_4$	218-19-	11.47	11.09
*12.	$^{a}C_{23}H_{29}N_3O_4$	204-05		

+ % Analysis found C, 66.6%, H, 7.35%, requires C, 67.3% ; H, 6.8%.

* % Analysis found C, 66.6%, H, 6.9%, requires C, 67.3% ; H, 6.8%.

Compounds recrystallised from . [a] Ethanol
[b] Methanol
[c] Methanol/Propanol
[d] Ethyl Acetate/Methanol

Yields of the compounds varied from 55-70%.

IR : 1. 3150(NH or OH), 2800-2900(CH_2), 1640(C=O), 1610(aryl).
2. 3200(NH or OH), 2800(CH_2), 1640(C=O), 1600(aryl).
3. 3130(NH or OH), 2800-2900(CH_2), 1638(C=O), 1600 (aryl)
4. 3140(NH or OH), 2800(CH_2), 1640(C=O), 1600 (aryl).
5. 3200(NH or OH), 2800(CH_2), 1640(C=O), 1604 (aryl).
6. 3240(NH or OH), 2930(CH_2), 1640(C=O), 1604 (aryl).

Bio-Assay :

Antibacterial Activity : Six compounds (4, 8, 9, 10, 11, 12) were tested against the strains of *Staphylococcus aureus*, *Bacillus subtilis* and *Sarcina lutea* by the reported agar diffusion method[13]. Compound No. 8 showed significant activity against *Staphylococcus aureus* ; others did not inhibit the growth of any strain.

Antiviral Activity : Six compounds (1, 2, 3, 5, 6, 7) were tested against Tobacco mosaic virus. Compounds 1, 3 and 6 showed significant inhibition *in vivo*. Others were inactive.

Acknowledgement

The authors are thankful to the Head of Chemistry Deptt., for department facilities. Thanks are also due to C.D.R.I., Lucknow for elemental analysis and IR spectra and to the Botany Deptt., Lucknow University for antiviral testing. One of the authors (MS) is thankful to C.S.I.R., Delhi, for financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 920-923

Epoxy Acids of *Mucuna prurita* Seed Oil**

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Manuscript received 26 March 1979, revised 6 September 1979, accepted 9 July 1980

Oil from the seed of *Mucuna prurita* (Leguminosae, Hindi, —Jangli Kawanch) contains previously unidentified *cis*-12, 13-epoxyoctadec-*trans*-9-enoic (1%) and the more common vernolic [*cis*-12, 13-epoxyoctadec-*cis*-9-enoic] (4%) acid. Gunstone's procedure of direct acetolysis of oil containing epoxy acids in minor amounts was adopted to characterize the epoxy acids in the oil. The techniques used in isolation and identification of the acids included thin-layer and column chromatography, IR, UV, NMR and chemical reactions (viz., reduction and oxidative cleavage) coupled with GLC.

M. prurita is a wild variety of species *M. pruriens*, which is cultivated for its brown valvety legumes and used as a vegetable. An early report[1] from this laboratory about 1.3% of epoxy acid in *M. pruriens* led to the present compositional study of an allied species. Fatty acid composition of the oil has been determined by chromatographic techniques.

Experimental

The presence of epoxy function was revealed by on-the-plate test with picric acid[2]. For determination of epoxyacyl content of oil, hydrogen bromide titration was performed at 3° by the procedure of Harris *et al*[3]. Analytical TLC was carried out on 0.25 mm layers of Silica Gel G developed in Et_2O-hexane-acetic acid (20 : 80 : 1, v/v/v). Dihydroxy acid methyl esters were analyzed by TLC on H_3BO_3-Si Gel G[4] and $AgNO_3$-Si Gel G[5] also. The spots were visualized by spraying with H_2SO_4-$K_2Cr_2O_7$ followed by charring. Mixed dihydroxy esters were fractionated by column chromatography using silver nitrate-impregnated silica using a mixture of ether in hexane in increasing proportions. GLC analyses of methyl esters were carried out as described by Miwa[6]. A Perkin-Elmer Model 154, equipped with thermal conductivity detector, using stainless steel packed column (2 m × 3 mm) coated with diethylene glycol succinate (DEGS, 15% on chromosorb W, 45-60 mesh) was employed. The separations were carried out at 100 and 200° chart speed 0.76 m/hr with a hydrogen flow of 70 ml/min. The dihydroxy esters were cleaved before and after hydrogenation by the permanganate-periodate method of von Rudloff[7] and the products were subsequently chromatographed on GLC columns after esterification. IR spectra were determined with Perkin-Elmer Model 621 spectrometer. NMR spectra were run in CCl_4 at 60 MHz with TMS as internal standard, chemical shifts are expressed in τ. A Beckman DK-2A instrument was used to determine UV spectra.

Oil was extracted from the ground seeds with petroleum ether (b.p. 40-60°) and the methyl esters prepared by NaOMe transesterification[8]. A portion of the oil was acetylated[9], saponified and acidified, the resulting acids were separated into oxygenated and non-oxygenated fractions by partitioning between 80% methanol and petroleum ether (b.p. 40-60°)[9]. The crude dihydroxy acids and non-oxygenated acids obtained from methanol and petroleum ether extracts respectively were esterified with 2% HCl in MeOH by refluxing for 2 hr. Composition of non-oxygenated methyl esters was determined by TLC-GLC.

The analytical values of seeds and oil, determined according to the procedures recommended by the AOCS method[11], are summarized in Table 1.

TABLE 1—ANALYTICAL DATA ON *M. prurita* SEEDS AND OIL

Oil%	4.2
Moisture%	5.6
Protein content N × 6.25%	30.0
Refractive index, n_D^{40}	1.4840
Iodine value (Wijs)	98.0
Saponification value	194.0
Oxirane oxygen, %	0.25
HBr equiv. (%epoxyoleic)	4.87
Unsaponifiable content%	2.8
Ultraviolet (UV)	Usual
Infrared (IR)	840 cm⁻¹

The non-oxygenated esters when analyzed by GLC, had the composition shown in Table 2.

Results and Discussion

The *M. prurita* seeds contained 4.2% oil (dry basis). The UV spectrum showed no conjugation in the oil and its methyl ester. The IR spectrum of

** The paper was accepted for the Annual Convention of Chemists, 1978, held at Waltair from Dec. 27 to 31, 1978.

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TABLE 2—FATTY ACID COMPOSITION OF *M. prurita* OIL

Component	%
16 : 0	21.0
18 : 0	2.7
18 : 1	16.8
18 : 2	46.1
18 : 3	8.4
Vernolic	4.0*
cis-12,13-epoxyoctadec-*trans*-9-enoic	1.0*

* Calculated with the help of HBr titration, partitioning, and column separation.

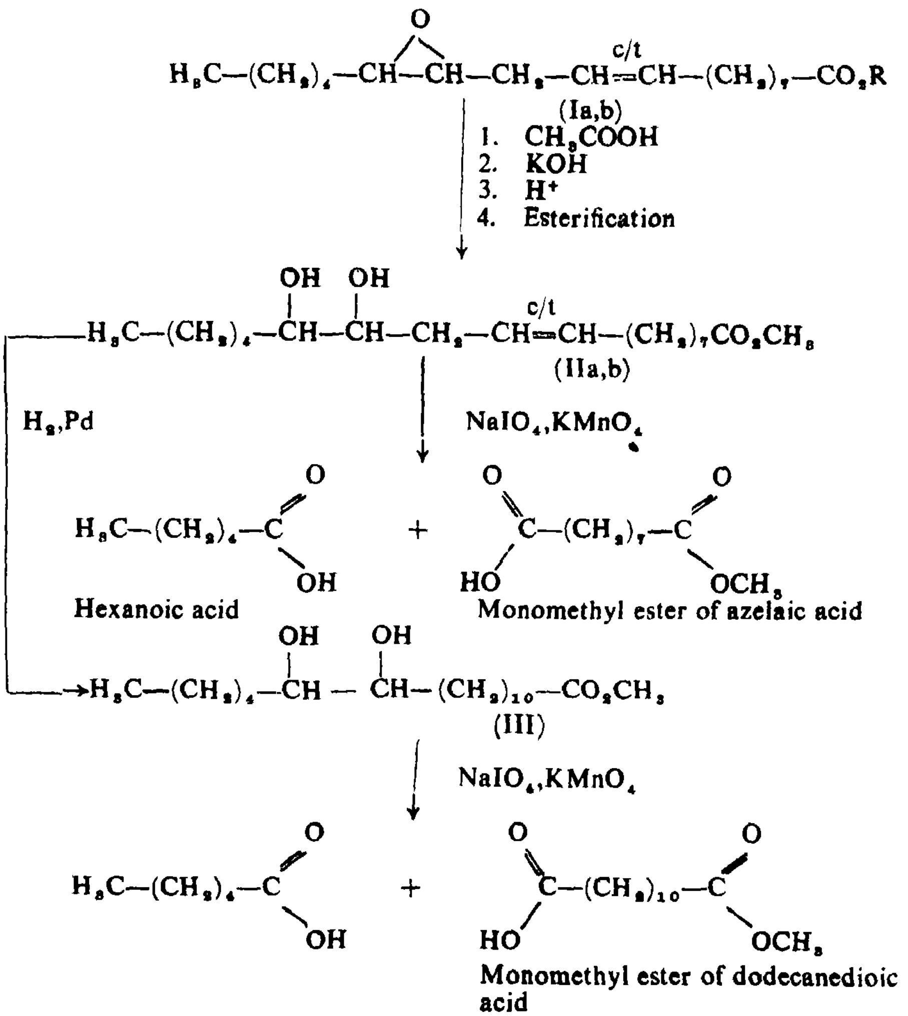
the oil showed a very weak band at 840 cm^{-1}, attributed to the epoxy group[10]. Picric acid TLC[8] also revealed the presence of epoxy function. The epoxy content in the oil was found to be 5% (based on HBr-titration and partitioning). The possibility for the occurrence of oxygenated acids other than epoxy in the oil was ruled out on the basis of IR and TLC.

Characterization of epoxy acids :

The epoxy acids of the oil were characterized as their corresponding dihydroxy acids formed by the direct acetolysis of oil followed by saponification[9]. The mixed dihydroxy esters on ordinary TLC migrated as a single spot whereas on Ag^+/TLC gave two spots differing in their R_f values. Separation of these mixed dihydroxy esters by argentation column chromatography gave two fractions (major Fraction 1, 80% : minor Fraction 2, 20% by wt. of the total hydroxy esters).

Characterization of Fraction 1 :

The structure of the major dihydroxy ester (Fraction 1) was established by elemental analysis,



R = diacyl glyceryl moiety ; Ia & IIa = *cis* double bond
Ib & IIb = *trans* double bond

Scheme 1

catalytical hydrogenation, oxidative cleavage, and comparison of its TLC, IR and NMR characteristics with that of an authentic sample of methyl *threo*-12,13-dihydroxyoctadec-*cis*-9-enoate prepared from *V. anthelmintica* seed oil by the same treatment. Anal. Calcd for $C_{19}H_{36}O_4$: C, 69.51 ; H, 10.97. Found : C, 69.84 ; H, 10.91. It absorbed one mole of hydrogen (one double bond). A co-TLC on ordinary, silver nitrate and boric acid-impregnated plates with an authentic sample showed the identity of the two dihydroxy esters. The IR and NMR spectra were superimposable with that of authentical sample. Permanganate-periodate cleavage[7] of this fraction as such and after hydrogenation also confirmed the proposed structure (Scheme 1). Therefore, the structure of Fraction 1 is established as methyl *threo*-12,13- dihydroxyoctadec-*cis*-9-enoate (IIa).

Characterization of Fraction 2 :

Anal. Calcd for $C_{19}H_{36}O_4$: C, 69.51 ; H, 10.97. Found : C, 69.45 ; H 11.0. Absorbed one mole of hydrogen (one double bond). On Ag^+/TLC Fraction 2 (minor) migrated ahead of Fraction 1 (major). Comparison of this fraction with that of the standard diol (from *V. anthelmintica*) by TLC on boric acid-impregnated Silica Gel G demonstrated that this had also *threo* configuration. The IR spectrum showed the bands at 3450 (due to $-OH$), 1740 (due to ester $-\overset{O}{\overset{\|}{C}}-$ group) and 970 (due to *trans* double bond) cm^{-1}. The ^1H NMR gave signals at τ 4.54 (2H, olefinic protons), 6.34 (s, 3H, ester methyl protons), 6.65 [4H. 2H ($-CH-O$)+ 2H($-OH$)], 7.76 (2H, α to the carbonyl function), 8.0 (protons α to the double bond), 8.7 (br, s, shielded methylene protons), 9.12 (rough t, 3H, terminal methyl protons). On D_2O shake the signal at τ 6.67 was reduced and integrated for two protons only (2H, $-CH-O$) indicating that the hydroxyl protons signal was merged with the signal of $-CH-O$. When subjected to splitting by permanganate-periodate[12] as such and after hydrogenation, the cleavage products were the same as in the case of Fraction 1 (Scheme 1). This indicated that the position of the hydroxyls and the double bond is the same in both the fractions. The presence of a distinct band near 960 cm^{-1} in the IR spectrum proves that the double bond is *trans* in this fraction. The most significant parameter in ^1H NMR for the determination of the configuration of a double bond is the coupling constant between the alkenyl protons. But in this case, as for most isolated double bonds, it is not possible to measure coupling constant[13], but a small chemical shift difference in alkenyl protons of Fraction 2 (τ 4.54) and authentic sample (τ 4.6) giving different and distinct absorption[13] is a conclusive evidence for the presence of *trans* and *cis* double bonds in Fraction 2 and authentic sample respectively. On the basis of elemental analysis, reduction, oxidative cleavage, direct argentation and boric acid TLC, IR and NMR data Fraction 2 was found to be methyl *threo*-12,13-dihydroxyoctadec-*trans*-9-enoate(IIb).

As no dihydroxy acid was obtained from the whole oil by solvent partition procedure when the acetolysis step is omitted, the dihydroxy acids are not present in the crude oil but must be formed by acetolysis of the epoxy acids. The presence of weak IR band at 970 cm^{-1} in the oxygenated oil concentrate showed that the acid with *trans* unsaturation is not an artifact formed during the chemical treatment of the oil (acetolysis followed by saponification) but is originally present in the oil.

The dihydroxy esters (Fraction 1 & 2) derived from the epoxy acids of *M. prurita* oil were identified as methyl *threo*-12,13-dihydroxyoctadec-*cis*-9-enoate(Ia) and methyl *threo*-12,13-dihydroxy-octadec-*trans*-9-enoate(Ib). These results demonstrate conclusively that the original epoxy acids are *cis*-12, 13-epoxyoctadec-*cis*-9-enoic (Vernolic) and *cis*-12,13-epoxyoctadec-*trans*-9-enoic acids.

Acknowledgement

The authors wish to express their sincere thanks to Prof. W. Rahman, Head, Department of Chemistry for providing necessary facilities ; M. Salauddin for GLC analysis ; H. L. Yadav for seed collection ; UGC and CSIR for rendering financial support to S. Q. Hasan and M.R.K. Sherwani respectively. This research was financed in part by a grant from the ICAR and Department of Science and Technology, New Delhi.

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Vol. LVII, September 1980, pp. 924-926

Search for Potent Anthelmintics—Part XV. Azomethines Derived from 2-Phenyl-3-(*p*-aminophenyl)-6, 8-Substituted Quinazolones

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Manuscript received 25 January 1980, accepted 26 July 1980

Thirty new 2-phenyl-3-(p-arylideneaminophenyl)-6,8-substituted-4-quinazolones have been prepared. Thirteen of them, when screened against *Hymenolepis nana* in mice at a dose of 250 mg/kg, showed significant activity.

A number of azomethines[1-3] have gained importance in recent years as potential anthelmintics. Nitrofurantoin[4], an azomethine has been particularly known to exhibit significant antifilarial activity against both adult females and microfilariae of *Litomosoides carinni*. Moreover, a few quinazolone derivatives[5] including 2-benzimidazolylmethylthio-4-quinazolones[6] have also shown marked anthelmintic activity against *N. dubius* infection in mice. These findings induced us to synthesise the title azomethines with a view to study their anthelmintic efficacy.

p-Phenylene diamine was heated with various substituted anthranils in open air bath to afford 2-phenyl-3-(*p*-aminophenyl)-6,8-substituted-4-quinazolones[a]. The latter were refluxed with different araldehydes in absolute ethanol in the presence of glacial acetic acid to furnish the desired azomethines.

Experimental

All melting points were determined in open capillary tubes and are uncorrected.

I. *2-Phenyl-3-(p-aminophenyl)-6,8-substituted-4-quinazolones :*

Equimolar quantities of an appropriately substituted anthranil and *p*-phenylene diamine were heated on a direct flame for 10 minutes. The reaction product was cooled and triturated with ethanol and filtered. The crude solid thus obtained was recrystallized from ethanol. Melting points, yield and analysis of the prepared compounds are recorded in Table 1.

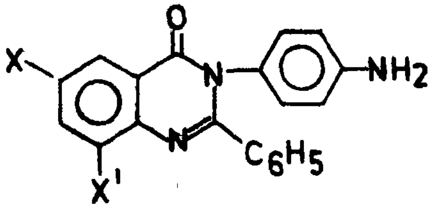
II. *2-Phenyl-3-(p-arylideneaminophenyl)-6,8-substituted-4-quinazolones :*

A mixture of 2-phenyl-3-(*p*-aminophenyl)-6,8-substituted-4-quinazolone (0.01 mole), araldehyde (0.01 mole), ethanol (30 ml) and glacial acetic acid (0.5 ml) was refluxed for 4 hours. The resulting mixture was cooled, filtered and excess of ethanol was distilled off from the filtrate. The solid obtained was recrystallised from ethanol (Table 2).

Determination of anthelmintic activity against H. nana *infection in mice :*

In vivo screening was carried out by the method of Steward, with slight modification. Newly weaned mice (25-20 g) were infected with 200 mature viable ova of *H. nana*. On the 15th day the infected animals were starved and treated next day with single oral dose of 250 mg/kg of the compound under test. A group of three animals was used for each of the compounds. Another group of three animals was left untreated as control. All the animals including controls were again starved for 24 hrs before they were sacrificed on the third day after treatment. The small intestine was removed and washed with saline water and worms were collected. The intestine was then pressed in between two glass plates and viewed against light. The worms which could not be removed by washing were counted. All the worms were classified according to their size and scored. The results, thus, obtained were compared with those of control group of animals.

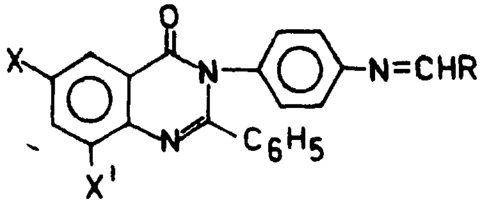
TABLE 1—2-PHENYL-3-(p-AMINOPHENYL)-6,8-SUBSTITUTED-4-QUINAZOLONES*



Sl. No.	X	X'	m.p. °C	Yield %	Molecular formula	Nitrogen% Found	Nitrogen% Calcd.
1.	H	H	290	60	$C_{20}H_{15}N_3O$	13.03	13.41
2.	Br	H	220	58	$C_{20}H_{14}BrN_3O$	11.01	10.71
3.	Cl	H	214	60	$C_{20}H_{14}ClN_3O$	12.38	12.00
4.	I	H	180	70	$C_{20}H_{14}IN_3O$	9.13	9.56
5.	Br	Br	270	52	$C_{20}H_{13}Br_2N_3O$	8.58	8.92

* Showed spectral bands at 1660 to 1670 cm^{-1} (C=O of quinazolones), 3400 to 3500 cm^{-1} (–NH– of arom prim. amine).

TABLE 2



Sl. No.	X	X'	R	m.p. °C	Yield %	Molecular formula	Nitrogen% Found	Nitrogen% Calcd.	% inhibition of *H. nana* in mice
1.*	H	H	C_6H_5	>300	50	$C_{27}H_{19}N_3O$	10.06	10.47	—
2.*	H	H	o-ClC_6H_4	>300	58	$C_{27}H_{18}ClN_3O$	9.92	9.64	—
3.*	H	H	p-ClC_6H_4	>300	56	$C_{27}H_{18}ClN_3O$	9.23	9.64	Inactive
4.*	H	H	o-OHC_6H_4	>300	62	$C_{27}H_{19}N_3O_2$	10.37	10.07	Inactive
5.*	H	H	p-OHC_6H_4	>300	64	$C_{27}H_{19}N_3O_2$	10.26	10.07	—
6.	H	H	p-$OCH_3C_6H_4$	>300	52	$C_{28}H_{21}N_3O_2$	9.43	9.74	—
7.*	Br	H	C_6H_5	170	68	$C_{27}H_{18}BrN_3O$	8.31	8.75	Inactive
8.*	Br	H	o-ClC_6H_4	192	70	$C_{27}H_{17}BrClN_3O$	8.52	8.16	.25
9.	Br	H	p-ClC_6H_4	184	70	$C_{27}H_{17}BrClN_3O$	7.80	8.16	65
10.	Br	H	o-OHC_6H_4	198	65	$C_{27}H_{18}BrN_3O_2$	8.94	8.47	—
11.	Br	H	p-OHC_6H_4	196	55	$C_{27}H_{18}BrN_3O_2$	8.32	8 47	—
12.	Br	H	p-$OCH_3C_6H_4$	180	52	$C_{28}H_{20}BrN_3O_2$	8.64	8.23	—
13.	Cl	H	C_6H_5	130	48	$C_{27}H_{18}ClN_3O$	9.31	9.64	—
14.	Cl	H	o-ClC_6H_4	162	50	$C_{27}H_{17}Cl_2N_3O$	8.68	8.94	12
15.	Cl	H	p-ClC_6H_4	144	48	$C_{27}H_{17}Cl_2N_3O$	8.62	8.94	—
16.	Cl	H	o-OHC_6H_4	200	60	$C_{27}H_{18}ClN_3O_2$	9.66	9.30	90
17.	Cl	H	p-OHC_6H_4	176	58	$C_{27}H_{18}ClN_3O_2$	9.00	9.30	30
18.	Cl	H	p-$OCH_3C_6H_4$	184	55	$C_{28}H_{20}ClN_3O_2$	9.41	9.02	—
19.	I	H	C_6H_5	235	62	$C_{27}H_{18}IN_3O$	7.64	7.97	—
20.	I	H	o-ClC_6H_4	220	46	$C_{27}H_{17}ClIN_3O$	7.82	7.48	55
21.	I	H	p-ClC_6H_4	198	50	$C_{27}H_{17}ClIN_3O$	7.06	7.48	—
22.	I	H	o-OHC_6H_4	242	52	$C_{27}H_{18}IN_3O_2$	8.00	7.73	54.1
23.	I	H	p-OHC_6H_4	224	46	$C_{27}H_{18}IN_3O_2$	7.42	7.73	—
24.	I	H	p-$OCH_3C_6H_4$	98	54	$C_{28}H_{20}IN_3O_2$	7.28	7.54	—
25.	Br	Br	C_6H_5	180	60	$C_{27}H_{17}Br_2N_3O$	7.16	7.51	—
26.	Br	Br	o-ClC_6H_4	177	64	$C_{27}H_{16}Br_2ClN_3O$	7.40	7.08	51.3
27.	Br	Br	p-ClC_6H_4	180	44	$C_{27}H_{16}Br_2ClN_3O$	7.39	7.08	—
28.	Br	Br	o-OHC_6H_4	184	50	$C_{27}H_{17}Br_2N_3O_2$	7.58	7.30	64.9
29.	Br	Br	p-OHC_6H_4	148	68	$C_{27}H_{17}Br_2N_3O_2$	7.02	7.30	42.2
30.	Br	Br	p-$OCH_3C_6H_4$	218	70	$C_{28}H_{19}Br_2N_3O_2$	7.46	7.13	—

* Showed spectral bands at 1680-1670 cm^{-1} (N=CH–).

The screening results are recorded in the Table 2.

Discussion

Thirteen compounds (Table 2), when screened against *H. nana* infection in mice at a dose of 250 mg/kg showed activity upto 90%. It was observed that the maximum activity was exhibited when OH in R was *o*-substituted. The activity was decreased when OH was *p*-substituted or replaced by Cl or H. Moreover, the presence of halogen in the phenyl nucleus of the quinazolone moiety was also essential for the activity in these compounds.

Acknowledgement

We thank the Head, Chemistry Department, Lucknow University for providing departmental facilities. One of us (S.N.M.) is also thankful to the C.S.I.R., New Delhi for the award of a Junior Research Fellowship.

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NOTES

Studies and Characterisation of the Heteropoly Ammonium Hexavanadomolybdate Dodecahydrate

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Manuscript received 2 February 1980, accepted 9 July 1980

A new heteropoly complex salt $(NH_4)_8[MoV_6O_{19}]\cdot 12H_2O$ has been synthesised and characterised by chemical and instrumental methods. The molecular weight of the heteropoly salt has been determined by determining cell dimension values by its X-ray powder diffraction studies. The powder file, with all the relevant data is furnished. The thermal depolymerization studies have been carriedout and the compound is found to be stable at 520±10°.

A few heteropoly vanadates have been reported[1]. But with the possible exception of 12-vanadophosphate anion[2], none of them has been well characterised nor their constitutions have been elucidated. The existence of isopoly anion $[V_6O_{19}]^{-8}$ has been distinctly confirmed in solution phase[3]. Considering the previous reports[4], detailed investigation is reported here for the solid state isolation, characterisation and thermal stability measurements of an interacted complex of molybdenum with $[V_6O_{19}]^{-8}$ anion.

Experimental

*p*H and thermometric titrimetric techniques[5], as discussed earlier[4], have been adopted to establish the conditions of formation of the heteropoly compound. Aqueous solutions of .2*M* ammonium metavanadate (NH_4VO_3) and .05*M* molybdic acid were found to be workable. When .05*M* molybdic acid was gradually added to 40 ml of .2*M* NH_4VO_3 solution, there was a gradual increase in *p*H upto the addition of 55 ml of molybdic acid. It was followed by a plateau of constant *p*H 5.3 upto 65 ml of molybdic acid. Thermometric titrations[5] corroborated the above results.

By comparing the results of *p*H and thermometric titrations from the graphs[4], the range in volume of the reactants could be studied. Hence 65 ml of .05*M* molybdic acid was slowly added to 40 ml of .2*M* NH_4VO_3 solution at 5° to 10° with constant stirring. The whole reaction mixture was kept at low temperature for three hours and then digested at a controlled temperature of 60° in a thermostat for six to eight hours till the volume reduced to half of its original. The mixture was then left for crystallization. After an interval of twelve days very small fibrous silky golden yellow crystals were collected which were further recrystallized from hot water. The complete analysis of the compound was done by chemical and instrumental methods. For estimation of molybdenum it was first separated[6] from vanadium (as it interferes) by precipitating molybdenum quantitatively as MoS_3 by passing a continuous flow of H_2S to the compound solution, mixed with 5 ml of formic acid at 0°. The solution was filtered, the precipitate containing MoS_3 was dissolved in minimum amount of concentrated HCl and a pinch of potassium perchlorate and then molybdenum was estimated as molybdenum oxinate[7]. Due to the above treatment V(V) is reduced[7] to V(IV), imparting a deep blue colouration to the filtrate. So vanadium was directly estimated from the solution by titrating it against .02(*N*) $KMnO_4$. The analytical values were corroborated by colorimetric determinations of molybdenum and vanadium by potassium thiocyanate and hydrogen peroxide methods[8] respectively. Nitrogen and hydrogen were estimated by element estimation technique. (Found : Mo, 9.992 ; V, 3 .451 ; N, 1.412 ; H, 3.318 per cent. Calcd. for $(NH_4)_8[MoV_6O_{19}]12H_2O$, Mo, 10.104 ; V, 31.936 ; N, 1.450 ; H, 3.340 per cent).

For assigning the molecular formula, from the above percentage composition data, the existence of complex anion $[V_6O_{19}]^{-8}$ was taken into consideration[3].

X-ray Powder Difference Studies :

Repeated attempts to isolate a sharp single crystal of the compound failed and so the X-ray powder diffraction technique[9] was applied for the determination of cell dimensions and consequently the molecular weight of the compound. The results of the powder photograph of the compound have been entered in the form of a standard powder file in the following table.

Analysing the above powder file, the system was found to be orthorhombic with $a=9.62\pm0.02$, $b=16.25+0.02$, $c=6.24$ Å and $\alpha=\beta=\gamma=90°$. So the volume V per unit cell was calculated to be 975.468 Å^3. The space group was uniquely established as D^2_{2h}-P_{nnn} from the following systematic presence of reflections : hkl = no condition ; okl = k+l

d	9.0	11.0	12.70	12.70
1/1	100	30	27	27

Ra CuK$_\lambda$ $\lambda = 1.5405$

Filter—Ni

1/1 visual strip measurement

Ref. Nil

System orthorhombic

$a = 9.62$, $b = 16.25$, $c = 6.24$ Å

$\alpha = \beta = \gamma = 90°$

Sign +

$D = 3.240$ gm l^{-1}

Colour—Yellow

Ref. Nil

Sample prepared in the laboratory

analyses show

Mo, 9.99 ; V, 31.45 ; N, 1.41 .

H, 3.31%

Pattern made at 25°C

$(NH_4)_2[MoV_6O_{19}]\,12H_2O$
Ammonium vanadomolybdate

dÅ	1/1	hkl	dÅ	1/1	hkl
12.7	27	200	3.20	2	511
11.0	30	201	3.13	3	311
10.0	15	111	3.10	26	600
9.0	100	210	3.03	25	152
8.5	25	021	3.00	7	610
7.7	25	121	2.95	8	313
7.0	25	331	2.90	2	040
6.0	2	221	2.79	25	132
5.9	10	400	2.75	8	620
5.5	10	102	2.70	2	444
5.4	25	420	2.62	2	532
5.3	2	521	2.45	25	332
5.1	2	212	2.41	2	440,402
4.9	2	202	2.33	3	422
4.75	10	022	2.30	2	622,623
4.75	2	402	2.23	3	521
4.13	6	040	2.07	2	630
3.75	25	302	2.03	3	533
3.65	2	222	2.865	8	621
3.50	2	511	1.835	2	131
3.45	2	220	1.72	3	250
3.39	2	331	1.62	4	042

$= 2n$; $hol = l + h = 2n$; $hkl = h + k = 2n$; $hoo = (h = 2n)$; $oko = (k = 2n)$; $col = (l = 2n)$ and $hkl = h + k + l = 2n$. The last condition gives the number of molecules in unit cell $Z = 2$. The observed density $\rho_{obs} = 3.240$ gm l^{-1} against the calculated density $\rho_{cal} = 3.259$ gm l^{-1}. From the relation $\rho_{obs} = \dfrac{1.66M.Z}{V}$, the molecular weight 'M' of the compound came to 951.9 against the theoretical value 957.65.

Thermal Depolymerization Studies :

The thermal depolymerization of the compound has been studied in the light of the investigations made by West and Audrieth[10] on a few heteropoly molybdates and tungstates. No reports on thermal depolymerization of heteropoly vanadates have been found in the chemical literature. The dissociation of the compound was observed at 130° when two molecules of water were eliminated which was confirmed by successive estimations. At 210° further two molecules of water along with two ammonia molecules were lost. The rest of the eight water molecules remained intact in the crystal lattice till 280°, above which they were completely removed. This work agreed closely with the work of Seroggie and Clark[11] on a few heteropoly salts. When the temperature was raised still higher, nearly at 520±10°, the compound was broken as a whole into the basic units of lower oxides of vanadium and molybdenum, which were confirmed by analysis. So the thermal stability of the compound is 520±10°.

Discussion

The generally accepted principle that condensation of heteropoly acids and salts depend upon hydrogen in concentration has further been corroborated as the complex anion of vanadomolybdate appearing within pH 5.3. X-ray powder diffraction studies helped to find out the molecular weight from which it has been possible to conclude that the compound is monomeric. The thermal depolymerization studies reveal four phase degradation leading to the end basic units of V_2O_5 and MoO_3. It is difficult to predict some idea about the configuration of $(NH_4)_2[MoV_6O_{19}]\,12H_2O$ as $[V_6O_{19}]^{-8}$ isopoly unit is a new entity and yet deserves exhaustive X-ray studies for its structure determination. Vanadium's presence in different variable oxidation states and due to its possibility of appearance in the form of irregular VO_4 or bipyramidal VO_5, it is not possible at present to predict anything regarding the structural arrangement of this compound.

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Synthesis of Some New Heteropoly Salts

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Manuscript received 3 January 1980, accepted 9 July 1980

In this communication three distinctly new heteropoly salts of molybdenum, vanadium and tungsten with 1 : 6, central : condensing atom ratio are reported.

The conditions of formations are the same as has been discussed in the previous communications[1,2]. The *p*H were maintained rigorously throughout the experiment.

6-Sodium tungstomanganate :

50 ml of .2*M* sodium tungstate, 45 ml of 0.05*M* manganese sulphate and 14 ml of glacial acetic acid were mixed together (*p*H 3.64), stirred vigorously for one hour, kept in a steam bath for three hours and left for crystallisation. Greyish white powdery compound was collected after an interval of seven days. The compound was analysed chemically and colorimetrically : (Found : Mn, 2.21 ; W, 48.23 ; Na, 1.00 ; H 2.25 ; calcd. for $Na_{10}[MnW_6O_{24}]28H_2O$: Mn, 2.41 ; W, 48.48 ; Na, 1.10 ; H, 2.45 per cent).

6-Ammonium molybdochromate :

Solutions of 50 ml of 0.05*M* ammonium molybdate, 40 ml of .05*M* potassium dichromate and 20 ml of glacial acetic acid were mixed together rapidly at *p*H 2.8, digested for three hours, evaporated to crystallisation on a water bath and left overnight ; orange coloured flaky powdery compound was separated after an interval of five days. From analysis : (Found : Cr, 4.02 ; Mo, 46.72 ; N, 6.62 ; H, 3.32 ; calcd. for : $(NH_4)_6$ $[CrMo_6O_{24}]$ $10H_2O$: Cr, 4.22 ; Mo, 46.90 ; N, 6.68 ; H, 3.58 ; per cent).

6-Potassium vanadochromate :

Solutions of 50 ml of .013*M* ammonium metavanadate, 43 ml of .05*M* potassium dichromate and 14 ml of glacial acetic acid were mixed by constant stirring (*p*H 2.4) for half an hour, digested for two hours and crystallised on a steam bath. After an interval of ten days brick-red shining crystals were collected from analysis : (Found : Cr, 5.22 ; V, 31.83 ; K, 8.03 ; H, 2.31 ; calcd. for $K_3[CrV_6O_{18}]12H_2O$: Cr, 5.43 ; V, 32.00 ; K, 8.15 ; H, 2.51 per cent).

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Mixed Ligand Complexes of Some Bipositive Cations with 6-Mercaptopurine and Thioguanine in Solution

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Manuscript received 28 January 1976, revised 7 May 1979, accepted 9 July 1980

6-MERCAPTOPURINE (MCP) and 2-amino-6-mercaptopurine (thioguanine, TGN) have been introduced in human cancer therapy, and has proved effective as anticancer agent in comparison to other purine derivatives like adenine and TGN. MCP and TGN having similar structures, form chelates with metal ions, which probably determine their activities.

The present communication deals with attempts to study mixed complexes of MCP and TGN with Co(II), Ni(II), Cu(II) and Zn(II), using 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy) as primary ligands. Studies with Cu(II) and Zn(II) were not possible.

Chelating reactions between the above metal ions and MCP have been described by Freiser *et al*[1], while TGN complexes with Be(II), Al(III), Cr(III), Pb(II), UO_2(VI), Ca(II) and Mg(II) have been reported earlier[2]. Formation constants of the mixed complexes have been determined using a modified form of Irving-Rossotti titration technique[3,4].

Experimental

All materials used were of reagent grade. Stock solutions (0.01*M*) of phen and bipy were prepared in water. 0.01*M* solutions of MCP and TGN were freshly prepared by dissolving in 0.02*M* alkali. Solutions of metal nitrates were prepared and standardized against EDTA[5].

*p*H measurements were done using an Elico *p*H meter (model LI-10) with glass (EK-62A) and calomel electrodes. The *p*H meter was calibrated with 0.05*M* potassium hydrogen phthalate solution.

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The *p*H meter reading was converted into hydrogen ion concentration using the method of Van Uitert and Haas[6].

Procedure : Mixtures for titrations were prepared as described earlier[10], using HNO_3, KNO_3, primary ligand and secondary ligand. The ionic strengths were 0.1*M* (KNO_3) and measurements were made at 25°, the media being 50% (v/v) ethanol. The alkali present in secondary ligand solution was preneutralized by equivalent amount of acid.

In the discussion the curves A to E represent those corresponding to the titrations of the various mixtures[10] (Figs. being omitted).

Results and Discussion

On being titrated phen, gives a sharp inflexion at $a=2$ (a = moles of KOH per mole of ligand) at lower *p*H. At higher *p*H, the secondary ligand curve(D) departs from the acid curve(A). When 1 : 1 metal+primary ligand solution was titrated, one inflexion at $a=2$ was observed which indicates the formation of a 1 : 1 complex in the lower *p*H region. In this system precipitation starts after $a=2$.

1 : 1 : 1 :: M : A : L solution on being titrated diverges from 1 : 1 MA curve(C) after *p*H 4, and precipitation starts after $a=3$. Curves E and C follow the same path upto *p*H~4, and then E diverges from C. When the formation of 1 : 1 MA is complete, the combination of L to MA takes place and additional alkali is required to neutralize the liberated protons due to the formation of mixed complex MAL.

The formation of the mixed complex is confirmed from a comparison of the theoretical composite curve and experimental curve, as well as from the observation that in the mixed ligand chelate titration curve E, no precipitation is observed upto $a=3$, while in the binary chelate, ML^+ precipitates in the very beginning.

The formation constant[7] was calculated from the following equation

$$K_{MAL} = \frac{\bar{n}_{MAL}}{(n-\bar{n}_{MAL})[L]^{n}_{MAL}} \quad (1)$$

the various quantities being obtained using method of Goldberg[8], the symbols having the usual meaning.

Only one protonation (pK = 7.85) constant has been evaluated in 50% (*v*/*v*) aqueous ethanol medium under the experimental conditions. The ionization of proton from neutral MCP occurs from the mercapto-group[9], while the second ionization from the imino group has not been observed, which appears to take place at a very high *p*H. Similarly, the ionization from TGN (pK = 8.63) is for the thio group.

Binary Cu(II) and Zn(II) complexes precipitate, and with MCP Cu(II) gets reduced to Cu(I)[1]. The binary chelates of all metal ions viz. Co(II), Ni(II) and Zn(II) with MCP or TGN are insoluble in 50% aqueous ethanol and could not be studied. The mixed ligand chelates with Co(II) and Ni(II) are soluble and their stability constants are reported in Table 1.

TABLE 1—FORMATION CONSTANTS OF MIXED LIGAND CHELATES IN 50% (*v*/*v*) ETHANOL (25°, μ=0.1*M*)

System	log K_{MAL}
Ni(II)-phen-MCP	5.21±0.01
Co(II)-phen-MCP	4.68±0.01
Ni(II)-phen-TGN	5.66±0.02
Co(II)-phen-TGN	5.18±0.01
Ni(II)-bipy-MCP	5.19±0.02
Co(II)-bipy-MCP	4.76±0.01
Ni(II)-bipy-TGN	5.61±0.01
Co(II)-bipy-TGN	5.17±0.01

Acknowledgement

The financial assistance received from Council of Scientific and Industrial Research is gratefully acknowledged.

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Formation Constants of Bipositive Metal Ion-Bipyridine-1-Hydroxy-2-Naphthoic Acid or 2-Hydroxy-1-Naphthoic Acid Complexes in Solution

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Manuscript received 2 January 1979, revised 5 May 1980, accepted 9 July 1980

THE present communication describes pH-metric studies[1,2] on ternary complexes of Cu(II), Ni(II) and Co(II) ions with 2,2-bipyridine (bipy) as a primary and 1-hydroxy-2-naphthoic acid (1, 2 HNA) or 2-hydroxy-1-naphthoic acid (2, 1 HNA) as a secondary ligand (L) in 50% v/v aqueous-ethanol medium at 25° and at an ionic strength 0.1 (KNO_3). The evaluation of first and second step formation constants (K_1 and K_2 respectively) of binary complexes in M-L systems under identical conditions has enabled a comparison with the corresponding values of ternary complexes ($K^{M.bipy}_{M.bipy.L}$)

Experimental

Solutions were prepared in double distilled CO_2 free water and all the chemicals were of AnalaR grade. Aqueous solutions of metal nitrates, nitric acid and potassium hydroxide were prepared and used after standardization[3]. Aqueous solutions of KNO_3, bipy and ethanolic solutions of 1, 2 HNA and 2, 1 HNA were prepared by direct weighing. pH-measurements were made using a Philips pH-meter (PR 9405M) with a glass-calomel electrode assembly at a constant temperature of 25°±0.1, in an inert atmosphere of nitrogen, and at an ionic strength 0.1 (KNO_3).

Procedure :

The following titration mixtures were prepared in each case and titrated individually against standard KOH solution ($N^\circ = 0.1042M$) : (A) $HNO_3 + KNO_3$, (B) mixture A+L, (C) mixture B+metal ion, (D) mixture A+bipy, (E) mixture D+metal ion, and (F) mixture E+L. The total volume was kept 50 ml ; the proportion of water and ethanol being adjusted to 50% v/v aqueous-ethanol media. In each case ionic strength was maintained by KNO_3 solution. The final concentrations in the binary systems were : $E^\circ = 0.002M$, $TC_L^\circ = 0.001M$ and $TC_M^\circ = 0.0002M$, while in the ternary systems these were : TC_{bipy}° (total initial concentration of bipy) $= TC_M^\circ = TC_L^\circ = 0.001M$; the concentrations of other components being the same as in the binary systems. All the symbols used have their usual meanings[1].

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Results and Discussion

The parameters $\bar{n}_A$, $\bar{n}$ and pL were evaluated to determine the protonation constants of the ligands and the formation constants of the binary complexes in M-L systems (Table 1). In M-L systems when L = 1,2-HNA, the $\bar{n}$ values extend over ≈0-1.8 in case of Cu(II) and Co(II) ions, but these do not exceed even unity with Ni(II) ion. Hence, Cu(II) and Co(II) form both 1 : 1 and 1 : 2 complexes, but Ni(II) forms only 1 : 1. In case of L = 2,1 HNA, while Cu(II) ions form both 1 : 1 and 1 : 2 complex species, Ni(II) and Co(II) form only 1 : 1. The stabilities of the metal complexes follow the trend : Cu(II) > Ni(II) > Co(II), which conforms to the Irving William's order. The stability order with respect to the ligands is 1,2 HNA > 2,1 HNA. In Ni(II) complexes, however, the values are identical within experimental error.

In M-bipy-L systems complete formation of $(M.bipy)^{2+}$ species occurs at pH ≤ 4.0 and remain stable at pH ≈ 6.0, 7.8 and 7.9 respectively in the cases of Cu(II), Ni(II) and Co(II) and thereafter the formation of hydroxo complexes appears likely. Subsequently precipitation takes place at pH ≈ 10.7, 8.7 and 8.3 for Cu(II), Ni(II) and Co(II) respectively. Thus, the average number of secondary ligand molecules attached per $(M.bipy)^{2+}$ ion ($\bar{n}_{mix}$) and free ligand exponent (pL_{mix}) were evaluated as described earlier[4-6], whereby the formation constants of ternary complexes were evaluated (Table 1).

TABLE 1—STABILITY CONSTANTS OF BINARY AND TERNARY METAL CHELATES (25°, μ = 0.1)

Reactions	log (equil. const.)
L – 1,2 HNA	
$L^{2-} + H^+ \rightleftharpoons LH^-$	11.78±0.03
$LH^- + H^+ \rightleftharpoons LH_2^0$	3.87±0.03
$Cu^{2+} + L^{2-} \rightleftharpoons CuL^0$	9.36±0.02
$CuL^0 + L^{2-} \rightleftharpoons CuL_2^{2-}$	7.01±0.02
$Ni^{2+} + L^{2-} \rightleftharpoons NiL^0$	6.99±0.02
$NiL^0 + L^{2-} \rightleftharpoons NiL_2^{2-}$	...
$Co^{2+} + L^{2-} \rightleftharpoons CoL^0$	6.86±0.02
$CoL^0 + L^{2-} \rightleftharpoons CoL_2^{2-}$	5.38±0.02
$(Cu.bipy)^{2+} + L^{2-} \rightleftharpoons (Cu.bipy.L)^0$	9.96±0.02
$(Ni.bipy)^{2+} + L^{2-} \rightleftharpoons (Ni.bipy.L)^0$	6.75±0.02
$(Co.bipy)^{2+} + L^{2-} \rightleftharpoons (Co.bipy.L)^0$	6.65±0.02
L – 2,1 HNA	
$L^{2-} + H^+ \rightleftharpoons LH^-$	11.38±0.01
$LH^- + H^+ \rightleftharpoons LH_2^0$	3.94±0.03
$Cu^{2} + L^{2-} \rightleftharpoons CuL^0$	8.68±0.02
$CuL^0 + L^{2-} \rightleftharpoons CuL_2^{2-}$	6.17±0.01
$Ni^{2+} + L^{2-} \rightleftharpoons NiL^0$	6.96±0.02
$NiL^0 + L^{2-} \rightleftharpoons NiL_2^{2-}$	...
$Co^{2+} + L^{2-} \rightleftharpoons CoL^0$	6.77±0.01
$CoL^0 + L^{2-} \rightleftharpoons CoL_2^{2-}$	...
$(Cu.bipy)^{2+} + L^{2-} \rightleftharpoons (Cu.bipy.L)^0$	8.98±0.02
$(Ni.bipy)^{2+} + L^{2-} \rightleftharpoons (Ni.bipy.L)^0$	6.85±0.02
$(Co.bipy)^{2+} + L^{2-} \rightleftharpoons (Co.bipy.L)^0$	6.20±0.03

Various factors affecting stability, structure and reactivity of ternary complexes in solution have been extensively dealt by Sigel[9]. From statistical considerations log $K^{M.\ bipy}_{M.\ bipy.\ L}$ is expected to be appreciably less than log K_1, as the concentration of electrons around the metal ion in $(M.\ bipy)^{2+}$ is more than in $[M(H_2O)_n]^{2+}$ owing to greater coordinating tendency of bipy than that of water. However, log $K_1 \approx$ log $K^{M.\ bipy}_{M.\ bipy\ L}$. This anomaly could perhaps be best explained in terms of indirect interactions (ternary complexes in which the two kinds of ligands 'simply' coordinate to the same metal ion), particularly by way of formation of π bonds[9]. There appears to be $M-N\pi$ interaction on account of back donation of the electrons from metal $d\pi$-orbital to the vacant delocalized π-orbital over the bipy molecule, in addition to the σ-bond between the two nitrogen atoms of the bipy molecule. Thus, the concentration of electrons around the metal ion in $(M.\ bipy)^{2+}$ does not increase significantly as a result of which electronegativity of the metal ion in this species remains almost the same as in $[M(H_2O)_n]^{2+}$, which justifies log $K_1 \approx$ log $K^{M.\ bipy}_{M\ bipy.\ L}$. On the other hand, log $K^{M.\ bipy}_{M.\ bipy.\ L} >$ log K_2, may be explained on the basis that during the formation of ML_2 species there is a coulombic repulsion between the negative oxygens of the two ligand anions tending to lower the stability of ML_2 specie, there is no such repulsion in the case of ternary complexes.

A plot of log $K^{M.\ bipy}_{M.\ bipy\ L}$ *versus* log K_1 is linear indicating that the process of association of L with $(M.\ bipy)^{2+}$ species in the ternary system, follows the same pattern as that of the association of L^{2-} with $[M(H_2O)_n]^{2+}$ in the corresponding binary system.

Acknowledgement

One of the authors (PKD) is thankful to the Principal, D.H.S.K. College, Dibrugarh, Assam for providing necessary facilities and for the grant of study leave towards the completion of this work.

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A Nickel(II) Complex of a New Hydrazone Type Macrocyclic Ligand

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Manuscript received 30 November 1979, accepted 9 July 1980

SINCE Melson and Busch[1] reported the efficacy of a metal ion, particularly nickel(II), indictating the synthesis of a macrocyclic ligand through self-condensation of *o*-amino benzaldehyde, a large number of reports have appeared in the literature concerning synthesis of metal chelates of a variety of macrocyclic ligand[2,3]. These macrocyclic ligands have all nitrogen[4], all sulphur[5], all oxygen[6], or nitrogen-sulphur[7] or nitrogen-oxygen as donor centres[8]. We wish to report here a nickel complex of a new macrocyclic ligand(III) prepared by the reaction of *bis*(acetyl acetone) ethylene diimine(II) with carbohydrazide(I) in presence of nickel(II) ion.

Experimental

Materials and Methods:

A. *Synthesis of the ligands :*

(i) *Ethyl ester of carbazic acid :* $H_2N-NH-COOC_2H_5$

Its synthesis and properties have already been described in an earlier paper from this laboratory[9].

(ii) *Preparation of carbohydrazide :* $NH_2-NH-CO-NH-NH_2$

This has been described earlier[9,10].

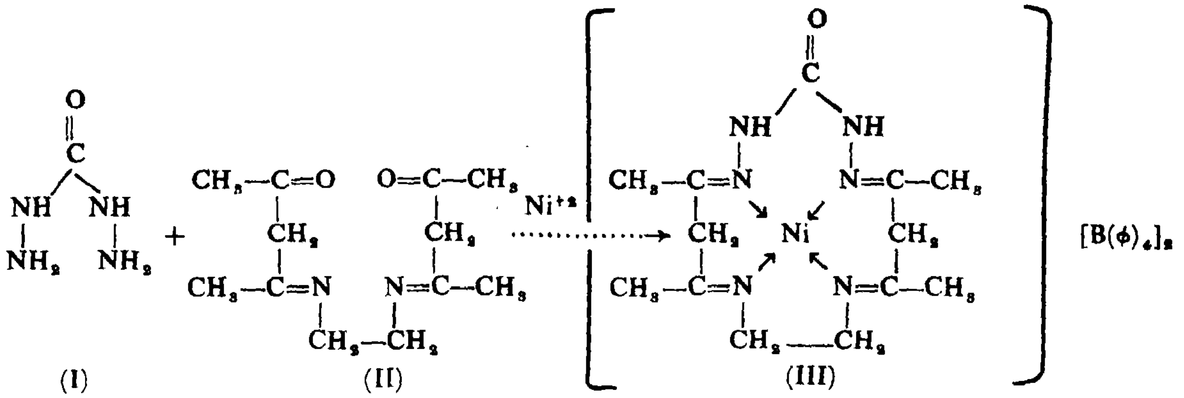
(iii) *Preparation of* bis(*acetylacetone*) *ethylene diimine :*

This Schiff base was prepared following standard procedure[11]. (m.p. 111°; lit., m.p. 111.5°).

B. *Synthesis of the complex :*

(i) *Preparation of tetraphenyl boron salt of the nickel(II) macrocyclic complex.*

Nickel(II) chloride hexahydrate (.005 mole, dissolved in 2 ml rectified spirit) was added to a hot



(I) (II) (III)

solution of the carbohydrazide (.005 mole) in 40 ml of boiling rectified spirit. During the addition, sky-blue coloured precipitate appeared immediately. This was refluxed for 5 minutes.

Then *bis*(acetylacetone) ethylene diimine (.005 mole, dissolved in 5 ml rectified spirit) was added to the mixture and refluxing was continued for 7 hours. The initial sky-blue precipitate went into solution with time and a reddish-green solution appeared. It was cooled to room temperature and filtered. The volume of reddish-green solution was reduced by evaporation to one-third. It was again cooled to room temperature and filtered again. The filtrate was treated with excess of anhydrous acetone. A sticky mass alongwith a red solution appeared. The sticky mass was repeatedly treated with anhydrous acetone till a crystalline product was obtained. This was filtered under suction and was washed with hot acetone and dried over silica gel. This crystalline compound was dissolved in rectified spirit and filtered. To this filtrate, appropriate amount of sodium tetraphenyl boron solution (in rectified spirit) was added.

After some time needle-shaped reddish-yellow crystalline product separated out. It was filtered, washed with warm rectified spirit and dried over silica gel.

Found for the dihydrate : N, 8.4 ; Ni, 5.6 ; H_2O 2.6 per cent.

Calc : N, 8.46 ; Ni, 5.9 ; H_2O, 3.0 per cent.

The sample was heated in an oven at 120°, cooled, and then again analysed.

Found : C, 75.45 ; H, 7.1 ; N, 8.7 and Ni 5.8 per cent.

Calc : C, 75.23 ; H, 6.4 ; N, 8.7 and Ni 6.03 per cent.

Analysis and physical measurements :

Nickel was estimated as *bis*(dimethyl glyoximate) nickel(II). Nitrogen was determined by Dumas method. Magnetic moment was obtained from corrected χ_M values, using a Gouy Balance with $CuSO_4.5H_2O$ as a calibrant. Nujol mull spectrum was run by R.S.I.C., Madras. Solution spectrum was run in Hilger-Uvispek spectrophotometer over the range 350-1000 nm. C & H analysis as also the I.R. spectra were carried out by C.D.R.I., Lucknow. The electrical conductivity was measured by Philips conductivity bridge at 25°.

Results and Discussion

A. *Infrared spectra :*

We have studied the i.r. spectra of *bis*(acetylacetone) ethylene diimine, carbohydrazide and nickel(II) complex of the new macrocyclic ligand.

The absorption bands of *bis*(acetylacetone) ethylene diimine agree quite well with those reported and assigned by Ueno and Martell[12]. The CH_2, CH_3 absorptions are found as weak and little broad bands within 2950 to 3150 cm^{-1} while the keto (C=O) and (C=N) appear at 1610 and 1580 cm^{-1} respectively. The carbohydrazide shows bands at 3360, 3200 and 3300 cm^{-1}. These are assigned as the asymmetric (N – H), symmetric (N – H) vibration of the – NH_2 group, and the secondary – NH group[13] respectively. The C=O stretch of the carbohydrazide appears as a strong broad absorption band centered at about 1635 cm^{-1}, while the C – N stretch[14] appears as a medium strong band at 915 cm^{-1}. In the nickel(II) macrocyclic complex, the proposed structure(III) calls for a secondary N – H stretch only. In keeping with this only one very strong sharp band appears at 3320 cm^{-1}. We assign this to the secondary N – H stretch. If all the four C=N nitrogens had similar environments and if all of them were coordinated to the metal ion (cf. III), we would have a single stretch for C=N. In reality, the i.r. spectrum of the complex distinctly shows one very strong and broad band centred at 1530 cm^{-1} which is assigned to C=N stretch in our complex. The broadness probably indicates that we have two different kinds of C=N in the complex. Compared to *bis*(acetylacetone) ethylene diimine the C=N stretch[15] at

1580 cm^{-1} we observe a lowering of 50 cm^{-1}. A sharp aromatic C–C stretch is observed at 1480 cm^{-1} due to the tetraphenyl boron anion. The carbonyl stretch (C=O) in the complex remains almost unchanged at 1630 cm^{-1} compared to that in the free carbohydrazide (1635 cm^{-1}). This small variation cannot be taken as an indication of its coordination to nickel(II). A critical study of the i.r. spectra of the three compounds (I, II, III) thus reveals that nickel(II) is coordinated to the macrocyclic ligand through its four C=N groups.

B. *Conductivity* :

In nitromethane, (.001 molar solution), the complex registers a value of 129 ohm^{-1} cm^2 mol^{-1} which is quite good for a bi-univalent electrolyte with a heavy anion like tetraphenyl boron[16].

C. *Electronic spectra and Magnetic properties* :

The macrocyclic complex crystallises with two molecules of water which could be removed at 120°. The anhydrous sample shows only one spectral band in the solid state at about 390 nm (25.6kK) which is indicative of a square planar $[NiN_4]$ chromophore[17,18]. The anhydrous sample was found to be diamagnetic. Interestingly, the hydrated complex shows a paramagnetic moment of 1.5 B.M. and its electronic spectrum is not well resolved. The solid crystalline hydrated complex probably indicates an equilibrium between the square planar dihydrate and pseudo-octahedral diaquo complex.

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Schiff Base Complexes of Some Transition Metals

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Manuscript received 7 January 1977, accepted 2 July 1979

SCHIFF bases have been widely used as complexing agents[1-3]. In the present communication, N-9-anthracylidene-*p*-dimethylaminoaniline (abbreviated as ADAA) has been used to isolate and characterise the chelate compounds of Ti(IV), Zr(IV), Hf(IV), Th(IV), Ni(II) and Co(II).

Experimental

The method of Kronke and Gross[4] was employed to prepare the Schiff base N-9-anthracylidene-*p*-dimethylaminoaniline by condensing 9-anthraceneglyoxal hydrate and *p*-dimethylaminoaniline in ethanolic medium, m.p. 78° (Found: C, 81.24; H, 5.46; N, 7.84; requires: C, 81.80; H, 5.68; N, 7.93 per cent). All the metal salts $TiCl_4$, $ZrCl_4$, $HfCl_4$, $ThCl_4$, $Ni(NO_3)_2$, $Ni(NCS)_2$, $Co(NO_3)_2$ and $Co(NCS)_2$ used were of A. R. quality.

Carbon, hydrogen and nitrogen analyses were carried out at the Microanalytical Laboratory, I.I.T., Kanpur. The conductance, magnetic and spectral studies were carried out by the reported methods[1-3]. Electronic spectra were studied both in solid state and in solution in acetone.

Isolation of Complexes :

Coloured solutions obtained on mixing equimolar solutions of the metal salts and the ligand in ethanol in stoichiometric ratio 1 : 2 (metal : ligand) were refluxed for 2.5-5.5 hr on steam bath. The reaction mixtures were cooled by refrigeration for few hours to few days and coloured crystals of the complexes were obtained which were washed with water, ethanol, ether and methylcyanide and dried in vacuum desiccator.

Analytical data, colour and physical properties of the complexes are cited in Table 1.

Results and Discussion

Ti(IV), Zr(IV), Hf(IV), Th(IV), Ni(II) and Co(II) form 1 : 2 (metal : ligand) complexes. All these complexes are insoluble in water but soluble in the organic solvents such as DMSO, DMF, NM, bromoform and benzene. Molar conductance measurements indicate that Ni(II) and Co(II) complexes are non-electrolytic in nature[5] whereas the other complexes exhibit biunivalent electrolytic

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TABLE 1—COLOUR, ANALYTICAL DATA AND PROPERTIES OF THE COMPLEXES

Sl. No.	Compound	Colour	% Elemental Analysis Calcd. (Found) C	Calcd. (Found) H	Calcd. (Found) N	Calcd. (Found) Halogen	Calcd. (Found) Metal	Molar Conductance λ_m ohm^{-1} cm^2 mole^{-1} (in NM)	μ_{eff} (B.M.)	Molecular weight (in Bromoform) Calcd.	Found
1.	$[Ti(C_{24}H_{20}N_2O)_2Cl_2]Cl_2$	Violet	64.43 (64.00)	4.47 (4.29)	6.26 (6.10)	15.89 (15.02)	5.36 (5.18)	175	0.11	894	875
2.	$[Zr(C_{24}H_{20}N_2O)_2Cl_2]Cl_2$	Blue	61.46 (61.08)	4.26 (4.19)	5.97 (5.78)	15.16 (15.00)	9.73 (9.68)	160	0.18	937	918
3.	$[Hf(C_{24}H_{20}N_2O)_2Cl_2]Cl_2$	Pink	52.96 (52.78)	3.90 (3.75)	5.46 (5.37)	13.06 (12.82)	17.44 (17.16)	182	0.22	918	902
4.	$[Th(C_{24}H_{20}N_2O)_2Cl_2]Cl_2$	Violet	52.90 (52.00)	3.68 (3.59)	5.15 (5.00)	13.04 (12.95)	21.04 (20.85)	158	0.28	1078	1056
5.	$[Ni(C_{24}H_{20}N_2O)_2(NO_3)_2]$	Bluish Green	66.95 (66.52)	4.51 (4.40)	9.47 (9.28)	—	6.62 (6.59)	50	2.72	886.7	872
6.	$[Ni(C_{24}H_{20}N_2O)_2(NCS)_2]$	Green	68.26 (68.00)	4.55 (4.42)	9.55 (9.36)	—	6.68 (6.59)	32	2.69	878.7	868
7.	$[Co(C_{24}H_{20}N_2O)_2(NO_3)_2]$	Pink	66.94 (66.49)	4.51 (4.42)	9.47 (9.51)	—	6.62 (6.56)	35	3.96	886.9	860
8.	$[Co(C_{24}H_{20}N_2O)_2(NCS)_2]$	Violet	68.24 (68.00)	4.55 (4.46)	9.55 (9.44)	—	6.68 (6.60)	28	4.02	878.9	870

nature[7,8]. Molecular weights determined by cryoscopic method using bromoform as the solvent are in good agreement with the calculated values.

Magnetic Studies :

Ti(IV), Zr(IV), Hf(IV) and Th(IV) complexes exhibit feeble paramagnetism (Table 1). Nitrate and thiocyanate complexes of Ni(II) and Co(II) show magnetic moments (Table 1) which are slightly lower than those usually for high spin octahedral complexes of Ni(II) and Co(II). A distortion from O_h symmetry is suggested ; this is further confirmed by the electronic spectral studies.

Electronic Spectral Studies :

The electronic spectra of $Ni(C_{24}H_{20}N_2O)_2(NO_3)_2$ and $Ni(C_{24}H_{20}N_2O)_2$ $(NCS)_2$ show bands at 9600, 12550, 17400, 29000 cm^{-1} and 8150, 12200, 15020, 26260 cm^{-1} respectively in solution whereas spectra in solid state exhibit peaks at 9560, 12510, 17385, 29100 cm^{-1} and 8125, 12190, 15000, 26400 cm^{-1} showing a close agreement. First two bands in each case may be due to the splitting of V_1 band because of the low symmetry of the ligand field transition whereas the last two bands characterise O_h symmetry.

The ratios ν_2/ν_1 for these complexes are 1.82 which are greater than the usual range 1.5-1.76 as reported[9] for the O_h symmetry, indicating thereby tetragonal distortion from O_h symmetry.

The difference of $(\nu_3 - \nu_2)$ calcd. and $(\nu_3 - \nu_2)$ obs. for octahedral symmetry is small but here this difference appears to be 6302 cm^{-1} and 6789 cm^{-1}. This difference is comparable to tetragonally distorted octahedral complexes[11].

The values of B calculated for the present complexes are 1173 cm^{-1} and 1122 cm^{-1} which are greater than the free ion value 1080 cm^{-1}. It may be assumed due to tetragonal distortion[11] of octahedral symmetry.

On the basis of the above facts it is concluded that the bands at 12550 cm^{-1} and 12200 cm^{-1} as experimentally observed are the low symmetry components. Therefore, for tetragonally distorted octahedral complexes with nitrate and thiocyanate ligands coordinated along Z-axis, the most favourable transitions for the first two bands are $^3B_{1g} \rightarrow {}^3E_g$ (9600 cm^{-1}, 8150 cm^{-1}) and $^3B_{1g} \rightarrow {}^3B_{2g}$ (12550 cm^{-1}, 12200 cm^{-1}) having energies 10 $D_q - \frac{35}{4}$ Dt and $10D_q^E$ in terms of radial parameters. The parameter Dt directly related to tetragonal distortion comes out to be 337 cm^{-1} and 463 cm^{-1}. The field along Z-axis is much weaker than along the xy plane as revealed by the parameters D_q (x,y), 1255 cm^{-1}, 1200 cm^{-1} and D_q(z), 295 cm^{-1}, 405 cm^{-1}, supporting thereby the reduced values of magnetic moments.

In the electronic spectra of Co(II) complexes in solution in acetone three bands at 8400, 8050 cm^{-1} $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) ; 18850, 18600 cm^{-1} $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and 24700, 24500 cm^{-1} $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) have been observed whereas the calculated band positions (ν_2) are 19100 cm^{-1} and 18737 cm^{-1} respectively which are in close agreement with the experimental band positions. It may be taken as a measure of tetragonal distortion[11-13] of O_h symmetry. Spectral bands of these two complexes in solid state appeared at 8350, 8125 cm^{-1} ; 18760, 18500 cm^{-1} and 24670, 24420 cm^{-1} which are identical to those as observed in solution state.

Splitting energy parameter (10 D_q), Racah parameter B and nephelauxetic ratio β of Co(II) complexes are 9830, 9408 cm^{-1} ; 1024, 980 cm^{-1} and 0.91, 0.87 respectively. Nephelauxetic ratio β happening due to the partial overlapping of 3d orbitals with orbitals of the ligand consists of both $f^2\sigma$ and $f^2\pi$, i.e. $f^2 = f^2\sigma\ f^2\pi$ and are 0.91 and 0.87, showing thereby the coincidency to the values as have been observed for tetragonally distorted[14] octahedral complexes of Co(II).

Infrared Spectral Studies :

I.R. spectra of the complexes as compared to that of the ligand show lowering of stretching frequencies of active carbonyl ($=C=O$) and azomethine ($-CH=N-$) groups such as 1700 cm^{-1} to 1630-1650 cm^{-1} and 1600 cm^{-1} to 1520-1560 cm^{-1} respectively, indicating the formation of complexes through these groups. Appearance of bands at 425-465 cm^{-1} and 475-550 cm^{-1} indicate the formation of metal-oxygen (M – O) and metal-nitrogen (M – N) bonds, supporting thereby chelation through oxygen and nitrogen atoms. However, peaks around 325-425 cm^{-1} are observed in the i.r. spectra of complexes of Ti(IV), Zr(IV), Hf(IV) and Th(IV), thus revealing the formation of metal-halogen (M – Cl) bonds.

The nitrate complexes of Ni(II) and Co(II) exhibit bands at 1290 cm^{-1} and 1280 cm^{-1} in their i.r. spectra, showing thereby that the complexes are nitrate-bonded[15].

The present thiocyanate complexes show i.r. bands at 2040, 2045 cm^{-1} and 800, 825 cm^{-1} indicating the coordination of thiocyanate ion with the metal ions through N-atom[16].

Acknowledgement

The authors are thankful to Dr. G. L. Maheshwari the retired Principal, S.S.V. College, Hapur for providing research facilities. Cooperation of Dr. R. C. Saxena and Dr. R. P. Mahesh is highly appreciated. Sincere thanks to U.G.C., New Delhi are gratefully acknowledged for providing financial assistance.

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Mn(II) and Cd(II) Complexes of Dicyandiamide

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Manuscript received 20 March 1979, revised 25 April 1980, accepted 9 July 1980

As a part of our programme of investigation on amide complexes of divalent metal ions, we have reported[1,2] complexes of lactams and nicotinamide. Dicyandiamide aroused our interest as it does not contain an oxygen donor atom even though four possible bonding sites are present. As a result, this communication reports a number of complexes of Mn(II) and Cd(II) with dicyandiamide.

Experimental

All the chemicals used are of AnalaR grade. Absolute ethanol solution of metal salts were reacted with ethanolic dicyandiamide solution in 1 : 2 proportion. On shaking compounds separated out in some cases, while in other cases compounds were precipitated after refluxing the solution for thirty minutes and keeping overnight.

Metal and nitrogen were estimated by standard methods. Conductance was measured in M/1000 acetone solution of the compounds. Magnetic moments of Mn(II) complexes were measured by Gouy method. I.R. spectra were recorded in nujol mulls using Unicam Sp-200 and electronic spectra by Unicam Sp-500 spectrophotometers with reflectance attachment. Relevant data are given in Table 1.

Results and Discussion

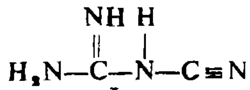
Conductance values of the compounds in acetone solution are low indicating non-electrolytic nature, except for the perchlorate complex which has Λ_M value ~ 250 mhos. cm^2 suggesting 1 : 2 electrolytic

TABLE 1—ANALYTICAL DATA OF Mn(II) AND Cd(II) COMPLEXES

	Compound	Colour	M.P. (°C)	Λ_M (Mhos. cm²)	%Metal Found	%Metal Calculated	%Nitrogen Found	%Nitrogen Calculated
1.	$MnCl_2(DCN)_2$	Light Pink	185	10.8	12.58	12.83	47.68	47.97
2.	$MnBr_2(DCN)_4$	Light Pink	206	8.4	10.45	10.78	40.02	40.30
3.	$Mn(NCS)_2(DCN)_4$	White	192	12.5	11.64	11.71	49.01	49.22
4.	$Mn(NO_3)_2(DCN)_4$	Light Pink	178	11.8	11.38	11.53	48.22	48.46
5.	$[Mn(DCN)_4](ClO_4)_2$	Light Pink	195	205	9.86	10.07	37.31	37.64
6.	$CdCl_2(DCN)_2$	White	196	6.8	31.71	31.99	31.62	31.87
7.	$CdBr_2(DCN)_2$	White	250	6.4	25.40	25.52	25.15	25.43
8.	$CdI_2(DCN)_2$	White	250	8.7	20.91	21.03	20.78	20.95
9.	$Cd(NO_3)_2(DCN)_2$	White	190	8.2	27.46	27.79	34.36	34.61
10.	$Cd(SCN)_2(DCN)_2$	White	202	11.8	28.06	28.35	35.08	35.32
11.	$[Cd(DCN)_4](ClO_4)_2$	White	205	213	23.12	23.44	46.55	46.72

nature. μ_{eff} values of Mn(II) complexes are ~5.9 B.M indicating a spin-free octahedral or tetrahedral configuration.

Dicyandiamide has the structure I



I

I.R. spectra of the ligand show several bands in the 3000-3350 cm^{-1} region attributable to $\nu(N-H)$. $\delta(NH)$ appears as a weak band at 1660 cm^{-1}. $\nu(C=N)$ is observed[8] at 1580 cm^{-1} and $\nu(C\equiv N)$ appears at 2170 cm^{-1}. In the complexes there is no splitting or shifting of these characteristic bands excepting $\nu(C\equiv N)$ which appears around 2220-2260 cm^{-1} region, suggesting that the ligand is bonded through the nitrile nitrogen atom. Strangely enough though there are four bonding sites, the ligand behaves as monodentate.

In the thiocyanato complexes of Mn(II) and Cd(II) a sharp band is observed at 2090 and 2130 cm^{-1} due to $\nu(C\equiv N)$ mode of thiocyanate suggesting[4] the presence of terminal N-bonded and terminal S-bonded thiocyanato group. In the nitrato complexes ν_4 and ν_1 bands occur at 1400 and 1280 cm^{-1} region respectively and the difference ($\nabla\nu$) is 120 cm^{-1} indicating[5-7] the presence of monodentate nitrato group. In case of the perchlorate complexes a broad band ~1100 cm^{-1} suggests[8-10] the ionic nature of perchlorate group, confirmed by molar conductance data.

Mn(II) complexes show absorption bands ~18.4.-18.6, 22.6-22.8, 24.8-25.3 and 27.8 K.K. regions assignable[11,12] to ν_1, ν_2, ν_3 and ν_4 transitions respectively, presumably indicating a high spin octahedral configuration. The perchlorate complex has bands at 20.4, 22.6, 23.8 and 26.6 K.K. regions suggesting[13,14] a possible tetrahedral geometry. On the basis of analysis, conductance and infrared spectral data cadmium complexes have a tetrahedral configuration.

Acknowledgement

Thanks are due to U. G. C., New Delhi for financial assistance.

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Separation and Estimation of Aluminium, Titanium and Iron in Bauxite by Paper Electrophoresis

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Manuscript received 14 February 1978, revised 22 August 1978, accepted 9 July 1980

ELECTROPHORETIC technique has been utilised for the quantitative separation of the main constituents of bauxite, as analysis of bauxite can be

achieved with a small amount of bauxite and within a very short time in comparison with the usual standard time consuming and laborious method of separation of bauxite[1,4].

Bauxite can be estimated spectrophotometrically after elution of the respective bands for aluminium, titanium and iron from electrophorogram. A drop of bauxite solution of known concentration had been subjected to paper electrophoresis using semimolar lactic acid[3] as carrier electrolyte. It was found that titanium(IV) moved towards anode, iron(III) and aluminium(III) moved towards cathode after electrophoresis.

Experimental

Preparation of migrant solution :

1.0898 gm of bauxite was decomposed by 10 ml conc. H_2SO_4 and 100 ml of water. After cooling, it was extracted by 100 ml of 6*N* (1 : 1) HCl and the volume of the solution was made upto 250 ml with 2*N* H_2SO_4.

Standard method for the analysis of the migrant solution :

Iron was estimated titrimetrically using standard dichromate as usual. Fe(III) and Ti(IV) can be determined together after reduction by passing through the Jone's reductor[4]. The amount of titanium (%) was then obtained by subtracting the amount of iron from the total amount of iron and titanium originally obtained in the volume of the migrant taken. Total quantity of Al_2O_3, Fe_2O_3 and TiO_2 can be determined gravimetrically[4]. The amount (%) of Al_2O_3 was then obtained by subtracting the amount of iron and titanium oxides from the amount of total oxides.

Paper electrophoresis of the migrant and Development of the electrophorogram :

Bauxite solution was electrophorised by using semimolar lactic acid. The zones of the migrants were identified with aqueous chromotropic acid for 'Ti' ; alizarin Red-S for 'Al', and potassium ferrocyanide for 'Fe'.

TABLE 1—DURRUM'S TYPE VERTICAL ELECTROPHORETIC INSTRUMENT[3] ; WHATMAN NO. 1 PAPER STRIPS (8 cm × 40 cm) ; POTENTIAL GRADIENT—2.5 volts/cm ; CARRIER ELECTROLYTE-SEMIMOLAR LACTIC ACID , TIME OF RUN 5½ HRS ; '+', '−' and ':' SIGN INDICATE MIGRATION TOWARDS THE ANODE, THE CATHODE AND THE POINT OF APPLICATION RESPECTIVELY

Migrant	Separation sequences of the migrants and the distance traversed by the zone in cm			
Bauxite	+Ti(IV)	:	Fe(III)	Al(III) −
	8 to 2.4		−0.2 to −1.5	−5.6 to −10.8

Estimation of Aluminium, Titanium and Iron :

After electrophoresis, the electrophorogram was dried and the portions of the strip containing aluminium, iron and titanium were cut out from the electrophorogram after matching said portions against the stained marked trip.

Aluminium (by Alizarin S) : The region of the strip containing aluminium was taken, eluted with 2*N* HCl. To the eluted solution, 0.1% alizarin Red-S, ammonium hydroxide and acetic acid were added and the volume made upto the mark with water.

Against the blank solution the optical density of the eluted aluminium solution was measured at the wave length of 510 mμ and found to be 0.026.

Titanium : Portion of the electrophorogram containing titanium was treated with 6*N* H_2SO_4 and the extraction of titanium ion was made with sulphuric acid, phosphoric acid followed by hydrogen peroxide in the same way as that of aluminium.

Against the blank solution the optical density of the eluted titanium solution was measured at 400 mμ and found to be 0.02.

Iron : The region of the strip containing iron was eluted with 2*N* hydrochloric acid by the same technique previously followed. To this solution 2*M* sodium acetate solution was added to bring the *p*H 3.5 ± 1. To this mixture hydroquinone, acetate buffer, (*pH* 4.5) and *o*-phenanthroline were added and the volume made upto the mark with water in 50 ml measuring flask.

Against the blank solution, the optical density of the eluted iron solution was measured after one hour at 510 mμ and found to be 0.03.

Standard solutions potassium of aluminium sulphate $KAl(SO_4)_2.12H_2O$ mol wt 474.7 for aluminium, potassium titanyl oxalate, $K_2TiO(C_2O_4)_2.2H_2O$ for titanium (standardised by standard potassium dichromate after passing through Jone's reductor) and A.R.

TABLE 2

Strength of alum solutions in terms of Al_2O_3 in molarity	O.D.	Strength of potassium titanyl oxalate in terms of TiO_2 in molarity	O.D.	Strength of ferric ammonium sulphate in terms of iron in molarity	O.D.
6.362×10^{-6}	0.024	1.43×10^{-4}	0.118	2.15×10^{-5}	0.21
7.635×10^{-6}	0.029	1.716×10^{-4}	0.146	4.62×10^{-5}	0.45
9.541×10^{-6}	0.035	2.002×10^{-4}	0.169	7.12×10^{-5}	0.69
12.78×10^{-6}	0.048	2.288×10^{-4}	0.192	9.72×10^{-5}	0.94
17.82×10^{-6}	0.068	2.575×10^{-4}	0.218	12.4×10^{-5}	1.20
		2.860×10^{-4}	0.240	14.88×10^{-5}	1.45
				17.36×10^{-5}	1.69

TABLE 3

Constituents in Bauxite solution	Optical densities of the eluted solutions after separation by Paper Electrophoresis	Concentrations of the eluted solutions calculated from the different calibration curves	Percentage of the constituents calculated from molar concentrations, volume of migrants, volume of dilutents and weight of Bauxite taken	Actual percentage of the constituents calculated by standard methodical analysis
Al_2O_3	0.026	6.9×10^{-8} Molar	53.8%	53.8%
TiO_2	0.02	0.24×10^{-4} Molar	11%	11.82%
Fe_2O_3	0.03	0.3×10^{-5} Molar	2.575%	2.5%

ferric ammonium sulphate (standardised by standard potassium dichromate) for iron were prepared. By taking different aliquot portions of these solutions calibration curve for aluminium, titanium and iron were drawn from the data as shown in the Table 2.

From the calibration curves of aluminium, titanium and iron the molar concentration of these eluted solutions were calculated and the percentages of Al_2O_3, TiO_2 and Fe_2O_3 in bauxite were calculated as given in the Table 3.

From the table 3, it shows that the technique can be equally utilised for the separation and estimation of aluminium, titanium and iron in bauxite.

Moreover, even with a micro amount of bauxite solution (4.32×10^{-5} gm in 0.01 ml of solution) and within few hours the estimation of the major constituents that is, iron, aluminium and titanium can be done easily without interference when usual standard methods are time consuming, laborious and special cares are to be taken to avoid interference.

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Magneto-Paper Electrophoresis in the Study of Inorganic Ions. Part. II*

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Manuscript received 19 January 1977, accepted 9 July 1980

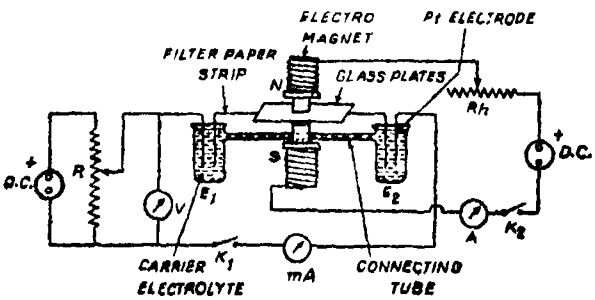
THE paper describes a comparative study of magnetophoresis, electrophoresis and magneto-electrophoresis with reference to paramagnetic inorganic ions, specially the lanthanide ions. A binodal curve similar to that obtained by plotting μ_{eff} (effective magnetic moments) of the lanthanide (+3) ions at 300°K against atomic number of lanthanons, supports the possible separation of lanthanons by magneto-paper electrophoresis method.

Comparative study :

Successful separation of various inorganic ions by magneto-paper electrophoresis[2] prompted us to undertake a comparative study of allied techniques[1].

Experimental

An apparatus[3] with minor modification in order to avoid the hydrostatic flow of the electrolyte, of the following type (Fig. 1) is used.



CIRCUIT DIAGRAM

Fig. 1.

In case of magnetophoresis the key K_1 is disconnected, so that there is no electric-field, whereas in case of electrophoresis the key K_2 is taken out

*Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, U. S. A., 1974. Part I, See H. G. Mukherjee and D. Majumder : *Z. Anal. Chem* 1975, **277**, 205.

when there is no magnetic-field in the circuit. Only in case of magneto-electrophoresis both the keys K_1, K_2 are connected to have both the electric- and the magnetic-field simultaneously in the circuit.

Whatman No. 1 filter paper is cut into strips of 1 cm × 35 cm. One drop of the aqueous solution of the ions, concentration being 0.5 mg/ml is placed on the central region of the paper previously marked with a lead-pencil. The paper is now moistened carefully with 0.1 *M* KCl and sandwiched between the glass-plates. This is then passed through the pole pieces of the electro-magnet and the paper ends are dipped into the carrier electrolyte. Then the necessary field is applied by connecting K_1 and/or K_2 keys. Both the potential difference and the strength of magnetic-field are kept steady by adjusting the rheostat R_h and resistance R. Individual ions are subjected to magnetophoresis, electrophoresis and magneto-electrophoresis successively for 25 minutes using 0.1*M* KCl as carrier electrolyte. After the experiment, the paper is air dried and then the migrants are located by spraying with proper developing agent.

TABLE 1

Ion	Magnetic moment[4]	Position of the central line of the band from the origin in mm			Developing agent
		Magneto-phoresis	Electro-phoresis	Magneto Electro-phoresis	
Cu^{+2}	1.8-2.2	3	17	15	Rubeanic Acid
Ni^{+2}	2.9-3.4	3.5	25	22	,,
Co^{+2}	4.4-5.2	2	28	26	,,
Fe^{+3}	5.0-5.5	2.5	35	32	$K_4Fe(CN)_6$
Mn^{2+}	5.2-6.0	2	31.5	25	NaOH
Cd^{+2}	0	2.5	18	18.5	$(NH_4)_2S_x$
$Fe(CN)_6^{3-}$	2.3	6	36	31	Fe^{2+}
$Fe(CN)_6^{4-}$	0	7.5	40	41	Fe^{3+}

p.d. : 160 volts ; Magnetic-field . 15 kilogauss ; Current . 1.5 amp.

From the result of the table 1, it appears that the magneto-paper-electrophoresis is a better tool in the study and separation of ions specially of paramagnetic ions. This new technique has been successfully applied for :

(a) Separation of paramagnetic ions from diamagnetic ones, e.g. ferricyanide has been separated from ferrocyanide in 20 minutes using 0.1*M* HCl as background electrolyte. Band position in mm : $Fe(CN)_6^{3-}$ 16 to 22 and $Fe(CN)_6^{4-}$ 30 to 35 towards anode. (b) Separation of high-spin complexes from low spin complexes of the same metal ions in the same valence state, e.g. ferriflouride from ferricyanide in 20 minutes using 0.1*M* KCl as carrier electrolyte. Band position in mm : FeF_6^{3-} 8 to 14 and $Fe(CN)_6^{3-}$ 18 to 22 towards anode. (c) Separation of lanthanid ions of different paramagnetism, e.g. La(III) from Gd(III) in 30 minutes using 0.05 citric acid as background electro lyte. Band position in mm : La^{3+} 0 to 5 and Gd^{3+} 12 to 16 towards cathode.

Study of Lanthanons :

The trivalent rare-earth nitrates are subjected to paper-electrophoresis for 30 minutes using 0.1*M* KNO_3 as background electrolyte. The same experiments are repeated in the magnetic-field. The difference in electromigration of the individual ions with (d_1) and without (d_2) magnetic-field are appreciable. The ratio $(d_2 - d_1)/d_2$ for each lanthanide (+3) ion is also included in Table 2.

TABLE 2

Lanthanide Ions (+3)	Electromigration distance of the central line of the band from origin in mm		$\frac{d_2 - d_1}{d_2}$
	In magnetic field (d_1)	Without magnetic field (d_2)	
La	22	24	.08
Ce	17	22	.23
Pr	15	23	.35
Nd	13	23	.43
Sm	17	23	.26
Eu	14	23	.39
Gd	6.5	23	.72
Tb	5.5	22	.75
Dy	5	24	.80
Ho	4.5	22.5	.80
Er	9.5	22	.57
Yb	13	24	.46
Lu	23	25	.08

p.d. . 160 volts , Magnetic-field : 15 kilogauss , Current : 1.5 amp.

The ratio $(d_2 - d_1)/d_2$ when plotted against the atomic number of the individual lanthanides, gives a curve[8], similar to that obtained by plotting μ_{eff} (effective magnetic moment) of the lanthanide (+3) ions at 300°K against the atomic number of the lanthanides (Fig. 2).

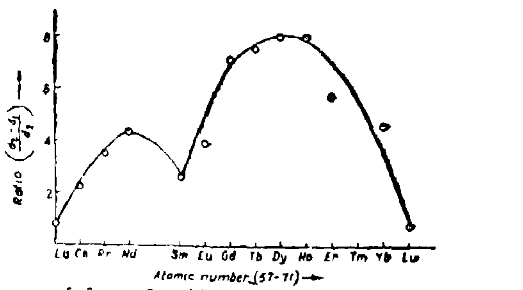


Fig 2 Bi-nodal curve of Lanthanone

Discussion

The application of an external magnetic-field with the electrophoresis influences the migration of the paramagnetic ions, which is retarded with increasing paramagnetism.

The possibility of the separation of the $Fe^{+3}-Cu^{+2}$, $Ni(NH_3)_4^{2+}-Co(NH_3)_6^{2+}$, $Fe(CN)_6^{3-}-Fe(CN)_6^{4-}$, etc. are thus due to the differences in their magnetic moments. Larger the strength of the magnetic-field, larger is the extent of diminution of migration of the particular paramagnetic ion. It is also evident that the separation of the paramagnetic

ions may even be possible by passing the zone chromatographically through the magnetic-field only, if the strength of the magnetic-field is considerably high (>>>15 kilogauss).

Acknowledgement

The authors appreciate useful suggestion of Prof. Michael Lederer of Rome during the progress of this work.

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Potentiometric Study of UO_2(VI) Salicylaldehyde System

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Manuscript received 14 August 1978, revised 23 April 1980, accepted 9 July 1980

URANYL chelates with phenolic compounds and carboxylic acids have been studied extensively[1-6]. In the present study the interactions of uranyl ion with salicylaldehyde in 75% (v/v) dioxane-water mixture at 30° and 0.1 *M* ($NaClO_4$) ionic strength have been investigated by Calvin-Bjerrum *p*H titration technique as modified by Irving and Rossotti. The effect of ionic strength on proton (*p*K) and metal ligand stability constant (log K) is observed by examining the system at μ=0.029 *M*, 0.049 *M*, 0.069 *M*, 0.089 *M* and 0.109 *M*. The influence of the solvent is studied by evaluating *p*K and log K values in 10%, 25%, 40%, 60% and 75% (v/v) dioxane-water mixtures.

All the reagents used were of AR quality. The method of purification of dioxane, the procedure employed and the methods used for the calculations of $\bar{n}_A$, $\bar{n}$, *p*K and log K are the same as given earlier[7].

Results and Discussion

*p*K and log K_1 values (Table 1) decrease with an increase of ionic strength. The data were analysed by the Bronsted equation

$$\log K = \log K^{\circ} + A\Delta Z^2 \sqrt{\mu}$$

The plots of *p*K and log K vs $\sqrt{\mu}$ were linear.

Table 1—Acid Dissociation Constants of Salicylaldehyde and Stability Constants of Uranyl Chelates with Salicylaldehyde

μ	*p*K	μ	log K_1
0.029	12.69	0.081	12.01
0.049	12.54	0.071	11.71
0.069	12.46	0.110	11.43
0.089	12.37		
0.109	12.31		

Accuracy 0.02 to 0.05.

Knowing A=6.78[8] the magnitude of ΔZ^2 was calculated which is given below:

Reaction	ΔZ^2 *values* *obs.*	*calc.*
$HL \rightleftharpoons H^+ + L^-$	−2.26	2
$UO_2^{2+} + HL \rightleftharpoons UO_2L^+ + H^+$	−2.07	2

By making use of modified Bronsted-Christian equation[8] $\log K = \log K^{\circ} + \frac{A\Delta Z^2 \sqrt{\mu}}{1+Ba\sqrt{\mu}}$ in which size of ions were obtained by trial method [a=7Å for salicylaldehyde, and a=6Å for UO_2(VI) salicylaldehyde], the observed linearity between *p*K vs $\frac{\sqrt{\mu}}{5.39\sqrt{\mu}}$ and log K, vs $\frac{\sqrt{\mu}}{1+4.62\sqrt{\mu}}$ for both systems respectively was much better than given by earlier plots. The plots gave value of $A\Delta Z^2$ for salicylaldehyde and for UO_2(VI)-salicylaldehyde as 13.54 and 13.11 respectively which did not show any appreciable improvement over the previous values.

The values of thermodynamic constants obtained from the plots of *p*K/log K vs $\frac{\sqrt{\mu}}{1+Ba\sqrt{\mu}}$ are in agreement with the theoretical values. These values are as follows:

Salicylaldehyde	$pK^{\circ} = 13.90$
UO_2(VI)-Salicylaldehyde	$\log K_1^{\circ} = 13.25$

Effect of the dielectric constant of the medium:

For the purpose of investigating the effect of dielectric constant on the complexation reaction, the two systems were studied in 10%, 25%, 60% and 75% (v/v) dioxane-water mixtures. The values of *p*K, log K_1 and log K_2 increase with an increase in the percentage of dioxane (Table 2). The plots of *p*K/log K_1 vs $\frac{1}{D}$ and plots of *p*K and log K_1 vs mole fraction are found to be linear.

TABLE 2—ACID DISSOCIATION CONSTANTS OF SALICYLALDEHYDE AND STABILITY CONSTANTS OF URANYL CHELATE WITH SALICYLALDEHYDE

Temp. = 30°C μ = 0.1M $NaClO_4$ Medium = 75% (v/v) dioxane-water

% Dioxane	Mole fraction	pK Practical	pK Thermodynamic	log K_1 Practical	log K_1 Thermodynamic	log K_2 Practical	log K_2 Thermodynamic
10	0.0296	8.53	8.64	6.68	6.79	5.88	5.99
25	0.0650	8.81	9.01	8.60	7.40	7.35	6.52
40	0.1233	9.16	9.51	7.18	8.13	6.66	7.01
60	0.2410	9.77	10.66	8.35	9.24	7.33	8.22
75	0.3870	10.15	12.03	9.26	11.16	8.11	10.01

Accuracy 0.02 to 0.05.

Calculation of the radius of the ion.

The effective ionic radius of the ligand anion was obtained by the Born equation[10]. The plot of $\Delta pK(pK_{mix}-pK_{water})$ against $\frac{1}{D}$ was found to be linear. The effective ionic radius obtained from the slope of the linear plot was 0.82Å for salicylaldehyde. The value observed is of the same order in magnitude as that obtained by Ohtaki[11] for oxalate and ammonium ions. The very low magnitude of the ionic radius may be due to the fact that this value does not give the size of the whole organic molecule but that of charged site, i.e. hydroxyl oxygen in salicylaldehyde molecule.

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Studies of Formation Constants of Lanthanoid Complexes with N-Benzoylphenyl Hydroxylamine

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Manuscript received 26 March 1980, accepted 9 July 1980

THE determination of the formation constant values for the rare earth complexes with organic ligands containing active oxygen atom have aroused interest because of the flexibility of the coordination number of the rare earth ions. In contrast, the nature of the lanthanide-hydroxamate bond interaction remained unexplored. In this paper, the formation constant values of five lanthanide ions with N-benzoylphenylhydroxylamine (N-BPHA), determined in dioxane-water medium (3 : 1 v/v), are reported.

The chemicals used were of either E. Merck, G. R., B.D.H. or AR grade. Doubly distilled water (CO_2 free) and purified dioxane[1] were used. The perchlorates of lanthanides used were prepared by digesting the corresponding oxides (99.9% pure, Johnson Matthey) with perchloric acid and removing the excess acid by repeated evaporation under an electrical heater. Finally the perchlorates were dissolved in water and made up to a definite volume. Lanthanide ions were determined by oxalate precipitation and their subsequent ignition to their respective oxides[2]. Free perchloric acid present in the metal perchlorate solutions were determined by running a known volume of the solution through a column of Amberlite IR – 120 (H^+ – form) and titrating the liberated acid with a standard sodium hydroxide solution.

N-Benzoylphenylhydroxylamine (N-BPHA) : The reagent was prepared by the method as described earlier[3]. Before use, the reagent was repeatedly

recrystallised. The purity of the reagent was verified by m.p. (121°) determination and matching of the IR spectra.

Procedure : The general procedure consisted in the titration under inert (nitrogen) atmosphere at 30°±0.5° with standard sodium hydroxide solution [4.197×10^{-2} *M* in 3 : 1 (v/v) dioxane-water medium] of a 40 ml dioxane-water (3 : 1 v/v) solution having a metal ion concentration $\sim 2 \times 10^{-3}M$, a reagent concentration $\sim 2 \times 10^{-2}M$, and sodium perchlorate in sufficient amount to maintain the initial ionic strength 0.1*M*. The *p*H-measurements were made with a Cambridge *p*H-meter having compatible glass (Universal type) and calomel electrodes connected by salt bridge. The dissociation constant of N-BPHA was determined in a similar manner. The *p*H-meter was calibrated in a way described by Van Uitert and Hass[4]. The *p*H-meter reading (B) was converted to the stoichiometric hydrogen ion concentration ($[H^+]$) using the relation

$$B = -\log [H^+] - \log U$$

where U is a function of the solvent composition and the ionic strength.

Calculation : Preliminary studies using two different concentrations of a metal ion keeping the metal to ligand ratio same revealed that no polynuclear complex species are formed. Moreover previous studies established the absence of hydroxo complex species in solution[5]. In order to determine the first two formation constants (K_1 and K_2) it was assumed that when $1 > \bar{n} > 0$, the concentration of tris- and other higher complex species in solution were negligible.

Under such condition eq. (1)

$$\sum_{n=0}^{N} (\bar{n} - n)[A^-]^n \beta_n = 0 \qquad \ldots (1)$$

may be rearranged to the linear form (2)

$$\frac{\bar{n}}{(1-\bar{n})[A^-]} = \frac{(2-\bar{n})[A^-]}{(1-\bar{n})} . K_1K_2 + K_1 \qquad \ldots (2)$$

Thus a plot of $\frac{\bar{n}}{(1-\bar{n})[A^-]}$ against $\frac{(2-\bar{n})[A^-]}{(1-\bar{n})}$ in the limiting condition $\bar{n}<1$ will provide a straight line from which K_1 is obtained as the intercept and K_1K_2 as the slope. Again assuming that at $2 > \bar{n} > 1$, the first three complex species coexist in solution but the concentration of the higher complex species are negligible. Eq. (1) then may be reduced to the linear form (3)

$$\frac{(\bar{n}-1)}{(2-n)[A^-]} + \frac{\bar{n}}{(2-\bar{n})K_1[A^-]^2} = \frac{(3-\bar{n})[A^-]}{(2-\bar{n})} K_2K_3 + K_2 \qquad \ldots (3)$$

K_1 having been already determined, the least squares fit gave K_2 and K_3 using the value of K_1 in eq. (3). The values presented in Table 1 represent the mean values of K_2 (both the plots for K_2 yielded values in reasonably good agreement).

The practical acid dissociation constant (pK_a) of NBPHA as determined by us came out to be 10.80. Tandon *et al*[6] reported the thermodynamic dissociation constant of N-BPHA in 1 : 1 aqueous-dioxane at 25° and 35° as 11.04 and 10.95 respectively.

TABLE 1—FORMATION CONSTANTS OF LANTHANIDE-N-BENZYLPHENYL HYDROXYLAMINE

Metal ion	1/r(Å^{-1})	Log K_1	Log K_2	Log K_3	Log β_3
La^{3+}	0.942	7.77	6.64	5.94	20.35
Pr^{3+}	0.987	8.10	7.49	6.60	22.19
Nd^{3+}	1.005	8.69	7.54	6.92	23.15
Sm^{3+}	1.037	9.38	8.16	7.18	24.72
Gd^{3+}	1.066	9.13	8.00	7.07	24.20

Table 1 shows the first three formation constant values of the five lanthanide ions. In general, for a given metal ion, $\log K_1 > \log K_2 > \log K_3$. However, the difference between any two consecutive constants is quite small, indicating that there is an almost equal tendency for all the complex species to coexist in solution. It is apparent from Table 1 that the log K_1 values gradually increases with increasing 1/r (in Å^{-1}) but in the case of Gd^{3+}-ion, it shows a decline. This is probably the change in aquo-ion structure and depression of class-b character in the heavier lanthanide ions which govern the sequence of formation constant values throughout the series[7,8]. Another cause of this anomaly may be some steric factors in N-BPHA molecule discriminating Gd^{3+} ion.

Acknowledgement

Thanks of the authors are due to Dr. M. Chaudhury of IACS for his help during this work.

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Spectrophotometric Determination of Ru(III) and Os(VIII) with 2,4,5-Triamino-6-Pyrimidinol

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Manuscript received 25 July 1978, revised 28 April 1980, accepted 9 July 1980

IN continuation of the studies reported earlier from this laboratory[1-3] the use of 2,4,5-triamino-6-pyrimidinol[4] for the colorimetric determination of Ru(III) and Os(VIII) is reported in this study.

Results and Discussion

Ruthenium : The broad experimental procedure for this work is as reported earlier[5]. Heating a 0.1 molar potassium chloride solution of a mixture of ruthenium (0.8-3 μg Ru/ml ; the optimum concentration range from a Ringbom plot) and 60 fold amounts of the reagent adjusted to a *p*H range of 4.0-5.0 for 20 min on a water bath gave a violet red coloured solution with λ_{max} at 570 nm useful for the determination of ruthenium at the specified range of concentration. The Sandell's sensitivity of the system is 0.0036 μg cm^{-2}. From 8 aliquots of standard solution containing 1.98 μg/ml of Ru, the standard deviation is 0.0050.

In determination of 2 μg/ml of ruthenium the tolerance of other ions (conc. in μg/ml) is found to be as follows : Br^-, ClO_4^-, BO_3^{3-}, PO_4^{3-} (1000) ; F^-, I^-, NO_3^-, EDTA (200) ; tartrate, citrate, (100) ; Ca^{2+}, Sr^{2+}, Ba^{2+}(400) ; Mg^{2+}, Cd^{2+}, Hg^{2+} (100) ; Mn^{2+}, Fe^{2+}, Zn^{2+} (60) ; Co^{2+}, Ni^{2+}, Pb^{2+} (30) ; Sn^{2+}, Pd^{2+}, Rh^{3+}, Ir^{3+}, Pt^{4+} and Os^{8+} (10). The presence of NO_2^-, CNS^-, $S_2O_3^{2-}$, $C_2O_4^{2-}$, thiourea, Ag^+, Cu^{2+} and Au^{3+} causes interferences.

Osmium : The reaction with osmium in the optimum *pH* range of 7.0-8.5 is found to be instantaneous and is complete with 30 fold concentration of the reagent. The optimum range of concentration is found to be 1.4-6.6 μg Os/ml for the spectrophotometric determination at a λ_{max} of 490-500 nm. The Sandell's sensitivity of the reaction is 0.007 μg Os cm^{-2}. The standard deviation is 0.003 for 8 aliquots of standard solutions containing 4.7 μg/ml of Os.

In the determination of 4.7 μg of Os/ml the tolerance of other ions (conc. in μg/ml) is found to be as follows : F^-, Br^-, CH_3COO^-, BO_3^{3-}, PO_4^{3-} (1000) ; I^-, NO_3^-, EDTA (500) ; CNS^-, citrate (250) ; Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+} (50) ; Zn^{2+}, Cd^{2+} ; Ru^{3+} (25) ; Mg^{2+} (20) ; Ag^+, Sn^{2+}, Rh^{3+}, Ir^{3+} and Au^{3+} (5). In case of Zn, Cd, Mg and Sn, the absorbance was noted after centrifuging off the precipitated species. Hg^{2+} (50 μg/ml) can co-exist in presence of 500 μg/ml of I^-. Zn^{2+}, Cd^{2+} (100) and Ni^{2+} (30) can be masked with EDTA and Co (30) with CNS^-. The presence of NO_2^-, $S_2O_8^{2-}$, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$, thiourea, Fe^{3+}, Pd^{2+}, Cu^{2+} causes serious interferences.

Of the substituted pyrimidines which have been developed for the spectrophotometric determination of ruthenium and osmium[6-9], the present compound is the most sensitive but however is not of high selectivity. The solution of the reagent is not very stable and needs to be prepared fresh.

Acknowledgement

The authors are grateful to Dr. G. R. Rao, IDPL, Hyderabad, for a gift sample of the ligand. One of us (P.J.) is also thankful to C.S.I.R. (New Delhi) for the award of Senior Research Fellowship.

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Some Physico-Chemical Studies on a Protein-Rich Fruit Seed (*Aegle marmelos* Correa)

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Manuscript received 21 March 1979, revised 2 February 1980, accepted 9 July 1980

THE tree, *Aegle marmelos* is found wild in Sub-Himalayan tracts, in central and south India and in Burma. The fruit is regarded as astringent, digestive and stomachic. It is also used in diarrhoea and dysentery[1]. The seed oil is reported to have purgative value[2]. In the present communication, chemical composition and sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS-PAGE) studies on different protein fractions of protein-rich seed kernel are described. This is the first time to report such a high-protein content of a fruit seed.

Materials and Methods :

Isolation of materials : The seeds were collected from the ripe fruits of the plant (*Aegle marmelos*) grown in West Bengal, India. Dried powdered seed kernel (10 g) was extracted with chloroform-methanol (3 : 1) at room temperature for 12 hr. The slurry was filtered. the residue was dried to yield defatted fraction (6.8 g approx.). From the filtrate the chloroform-methanol was evaporated off to yield the seed oil fractions (3.2 g approx.). The defatted material was extracted with water at room temperature and filtered. The filtrate was reduced to a smaller volume and the water soluble fraction was precipitated with ethanol. The yield of this fraction was 2 to 3% of the defatted fraction.

Analytical methods : Protein was estimated by the method of Lowry *et al*[3] by using bovine serum albumin (Sigma Chemical) as standard and also the protein-nitrogen was estimated by micro-Kjeldahl method. SDS-polyacrylamide gel electrophoresis (7.5%) was carried out following in general the method of Weber and Osborn[4], the gel system was calibrated using the following standard proteins : bovine serum albumin (67000), ovalbumin (43000), chymotrypsinogen (25000), myoglobin (17800) and cytochrome C (12400). For preparation of the sample, 10 mg of the seed fraction was added to 5 ml of 0.01 *M* sodium phosphate buffer (*p*H 7.2) containing 1% SDS and 1% β-mercaptoethanol. The mixture was heated at 100° for 3 min and then 20-25 μl of the mixture with 20% sucrose and 0.003% bromophenol blue applied to the gel.

The fatty acid content of the seed oil was estimated by the method of Haskins[5]. The fatty acids mixtures on treatment with ethereal diazomethane yielded the methyl esters of fatty acids. Gas liquid chromatographic (GLC) analysis of these methyl esters were carried out with a Hewlett Packard Model 5730A gas chromatograph fitted with a FID detector. Nitrogen was used as carrier gas. A $6' \times \frac{1}{4}''$ OD column containing 10% Apeizone on chromsorb WHP was used for the detection of fatty acids. The analysis was carried out against a standard mixture of fatty acids methyl esters.

Total carbohydrate was estimated by the method of Dubois *et al*[6], using D-glucose as standard. The following solvents were used for descending paper chromatography of sugars : (a) ethylacetate-pyridine-water (8 : 2 : 1) ; (b) *n*-butanol-pyridine-water (6 : 4 : 3). Whatman No 1 chromatography paper was used. Spray reagents were : (i) saturated solution of aniline oxalate in water and (ii) aniline hydrogen pthalate.

Results and Discussion

Chemical analysis revealed that the seed contained 62% protein (water soluble 2% and 60%, insoluble), 32% oil, 3% carbohydrate and 3% ash. The figures presented were the average of four independent estimations. The percentage of protein content of the seed was found to be the same by application of both Lowry *et al*[3] and Kjeldahl methods. The remarkably high protein content was found to be 32 to 42% in soyabean (*Glycine max*, L), whereas this seed contains 62% protein.

SDS-PAGE (Fig. 1a) of the defatted seed preparation gives 7 bands of respective MWS 110000, 106000, 80000, 60000, 36000, 20000 and 14500 daltons, which may be due to either seven different proteins or different subunits of some protein(s). Of these, only three components comprised the major fractions of the seed proteins. It was interesting to note that the water-soluble fraction (2-3% of defatted seed which contained 95% protein) revealed only single band of average MW 18000 daltons (Fig. 1b). Evidence of the single band was also confirmed by applying more than 100 μg of the sample per gel under identical conditions (Fig. 1c). This single protein band clearly indicated the presence of one subunit. This fraction on hydrolysis with $N-H_2SO_4$ yielded D-galactose, L-arabinose and D-xylose. Further studies are under progress to find out whether this protein fraction is a glycoprotein or a single polypeptide chain containing more than one subunit or it is a mechanical mixture of protein and polysaccharide. Amino acids composition of this protein is also under study. The hydrolysate of whole seed kernel was also found to contain the same sugars. As mentioned previously the seed oil was found to be 32% in which 28% was fatty acids. The fatty acid of the tolal seed oil were identified as palmitic acid,

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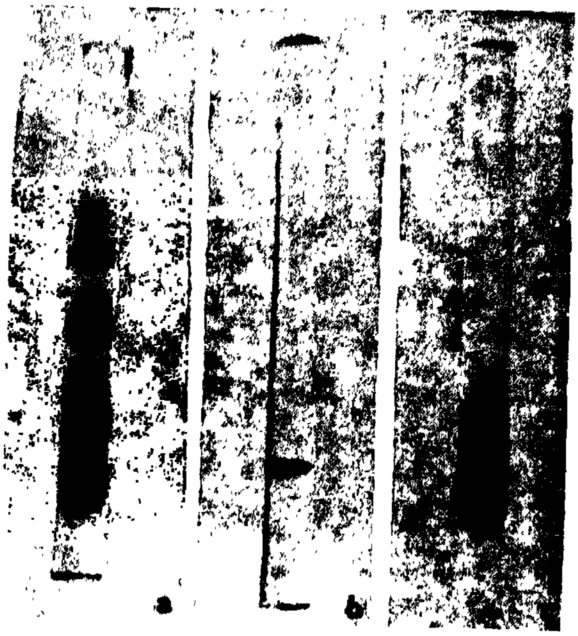


Fig. 1. SDS-polyacrilamide gel electrophoresis pattern of defatted seed protein fraction 50μg (a), and water-soluble fraction of defatted seed, 15μg (b) and 100μg (c).

stearic acid, oleic acid, linoleic acid and linonelic acid using GLC by converting them into their respective methyl-esters. The non-fatty acid fraction isolated from this was found to contain β-sitosterol (m.p. 137-38 and $[\alpha]_D^{28}$ 35) and an unidentified compound. The seed oil is reported to have some purgative effect[9] which needs some pharmacological studies. Considering all the above mentioned remarkable characteristics of the seed kernel, further studies on it are in progress.

Acknowledgement

The authors thank Mr. A. K. Das and Mr. S. N. Dey of this Institute for their technical assistance.

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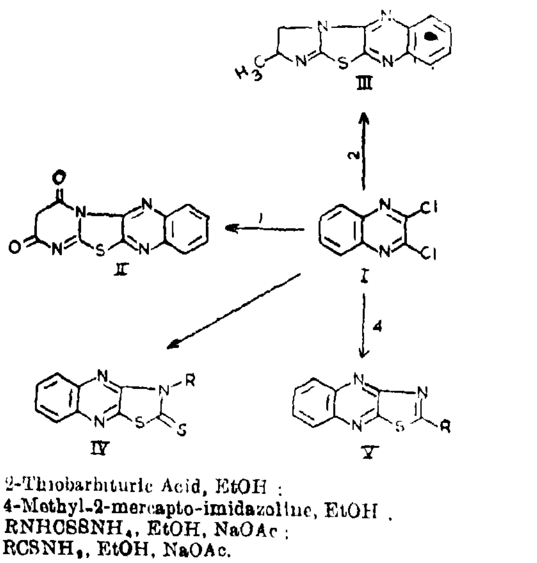
Heterocyclic Systems, Part I. Reactions of 2, 3-Dichloroquinoxaline with Cyclic Thioureas, Dithiocarbamates and Thioamides

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Manuscript received 7 May 1979, revised 10 October 1979, accepted 9 July 1980

In continuation to our earlier work[1,2], now syntheses of II, III, IV and V have been accomplished. I when condensed with 2-thiobarbituric acid in absolute alcohol yielded II, whereas with 4-methyl-2-mercapto imidazoline furnished III. Since 4-methyl-2-mercapto imidazoline is an unsymmetrical thiourea it is likely to yield 2-methyl-2,3-dihydro imidazo[2',1' : 2,3]thiazolo[4,5-b] quinoxaline(III) or its 3-methyl isomer. However since only one compound was obtained (TLC), it has been assigned the structure (III) on analogy with our earlier work[3], but needs confirmation. Thiazolo-quinoxalines (IV) and (V) were synthesized by the reactions of I with substituted ammonium dithiocarbamates and thioamides in presence of fused sodium acetate in absolute ethanol. Structures II, III, IV and V have been characterized by IR spectra (*vide* experimental).



1. 2-Thiobarbituric Acid, EtOH ;
2. 4-Methyl-2-mercapto-imidazoline, EtOH ,
3. $RNHCSSNH_4$, EtOH, NaOAc ;
4. $RCSNH_2$, EtOH, NaOAc.

Experimental

Melting points are uncorrected. IR spectra were taken in Nujol mull. TLC was performed on silicagel plates using acetone-benzene (1 : 3) as solvent system.

3H-Pyrimidino[2',1' : 2,3]thiazolo [4,5-b]quinoxaline-2,4-dione (II) :

A solution of I (1.00 g, 0.005 mole) and 2-thiobarbituric acid (0.72 g, 0.005 mole) in anhydrous

* For correspondence.

ethanol (25 ml) was refluxed on a steam bath for about 6-7 hours. The reaction mixture acquired orange colour and an orange-brown solid separated, which was filtered, washed with 5% sodium bicarbonate solution and finally with water. The compound was purified by dissolving in sodium carbonate solution and then reprecipitating with acetic acid, m.p. >290°, yield 0.6 g (44%), ν_{max} (cm^{-1}) 1710, 1650, 1600, 1530, 1150, 755. (Found: S, 11.34; N, 20.46. Calcd. for $C_{12}H_6N_4SO_2$, S, 11.85; N, 20.74%).

2-Methyl-2, 3-dihydro-imidazo[2'. 1' : 2, 3]thiazolo [4,5-b]quinoxaline(III) :

A solution of I (1.00 g, 0.005 mole) and 4-methyl-2-mercapto imidazoline (0.58 g, 0.005 mole) in absolute ethanol (25 ml) was heated on a steam bath for about 5 hours. The yellow coloured solid thus obtained was filtered, washed with sodium bicarbonate solution and then with water. Crystallization from DMF afforded yellow micro-needles, m.p.>300°, yield 0.4 g (33%), ν_{max} (cm^{-1}) 1610, 1555, 1335, 1260, 1120, 755. (Found: S, 12.92. Calcd. for $C_{12}H_{10}N_4S$, S, 13.22%).

2-Thio-thiazolino[4,5-b] quinoxaline(IV, R=H) :

It was prepared by refluxing a solution of I (1.0 g, 0.005 mole), ammonium dithiocarbamate (0.55 g, 0.005 mole), and anhydrous sodium acetate (0.82 g) in absolute ethanol (30 ml) for 3 hours. The yellow coloured solid was filtered, washed with water and crystallized from DMF m.p.>300°, yield 0.7 g (64%), ν_{max} (cm^{-1}) 3170, 3190, 1615, 1570, 1150, 835, 740. (Found: S, 28.84. Calcd. for $C_9H_5N_3S_2$, S, 29.22%). Similarly were prepared IV(R=o-HO-C_6H_4), m.p.>290°, ν_{max} (cm^{-1}) 3170-3040, 1610, 1555, 1265, 1140, 825, 755. (Found: S, 20.14. Calcd. for $C_{15}H_9N_3S_2O$, S, 20.58%). IV(R=$H_3CO-C_6H_4$), m.p.>290°, (Found: S, 19.95, Calcd. for $C_{16}H_{11}N_3S_2O$, S, 19.69%).

Thiazolo [4,5-b] quinoxaline V(R=H) :

It was synthesized by reacting equimolecular proportions of I and thioamides in presence of anhydrous sodium acetate in ethanol in the manner described above m.p.>280°, ν_{max} (cm^{-1}) 3100, 1610, 1485, 1330, 1160, 755. (Found: S, 16.68, Calcd. for $C_9H_5N_3S$, S, 17.11%). Similarly were prepared V(R=CH_3), m.p.>290° (Found: S, 16.33. Calcd. for $C_{10}S_7N_3S$, S, 15.92%), V(R=C_6H_5), m.p.>290 (Found: S, 11.87. Calcd. for $C_{15}H_9N_3S$, S, 12.16%). V(R=m-$NO_2-C_6H_4$), m.p.>290 (Found: S, 9.86. Calcd. for $C_{15}H_8N_4SO_2$, S, 10.39%).

Acknowledgement

The authors wish to express their sincere thanks to Prof. H. K. Pujari, Department of Chemistry, Kurukshetra University, Kurukshetra, to Dr. M. R. Bhandari, Principal, Government Post-graduate College, Churu, for encouragement and to the University Grants Commission, New Delhi for financial assistance.

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Synthesis of O, O-Dialkyl-S-[3-(Aryloxymethyl)-4-Substituted Phenyl-1,2,4-Triazol-5-yl]-Dithiophosphate as Possible Acetylcholinesterase (AChE) Inhibitors and Bactericides

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Manuscript received 23 July 1979, revised 25 February 1980, accepted 9 July 1980

ORGANOPHOSPHATES have been extensively used as insecticides[1,2] and exhibit antiacetylcholinesterase activities[3,4]. A number of substituted triazoles are good bactericides[5,6], fungicides[7-9] and herbicides[10,11]. Triazoles with phenoxymethyl moiety are expected to have increased pesticidal activities as phenoxy acetic acid itself has been associated with various biological activities[12,13]. In the present communication we have condensed several substituted triazoles with O,O-dialkyl chlorothiophosphate in order to synthesise O,O-dialkyl-S-[3-(aryloxymethyl)-4-substituted phenyl-1,2,4-triazol-5-yl]-dithiophosphates (I, Table 1) and tested for their biological activities.

Experimental

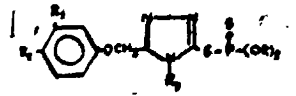
Melting points were taken in open capillaries and are uncorrected. The synthesised compounds have been characterised by ir spectroscopy and elemental analysis.

O, O-Dialkylchlorothiophosphate was prepared by known method of Fletcher *et al*[14]. Thiophosphoryl chloride was prepared according to the method of Moellar[15]. The key intermediate substituted triazoles have been prepared by known procedure[16].

O,O-Dialkyl-S-[3-(4-Chlorophenoxymethyl)-4-Phenyl-1,2,4-triazol-5-yl]-dithiophosphate :

O,O-Dialkylchlorothiophosphate (0.01 *M*) and 3-(4-chlorophenoxymethyl)-5-mercapto-4-phenyl-1,2,4-triazole (0.01*M*) was refluxed in dry acetone

Table 1—Physical Data and Antibacterial Activity of O,O-Dialkyl S-[3-(Aryloxymethyl)-4-Substituted Phenyl-1,2,4-Triazol-5-yl]-Dithiophosphates



Sl. No.	R_1	R_2	R_3	R	m.p. °C	Molecular Formula	Bactericidal Activity: *S. aureus*	Bactericidal Activity: *B. pumilus*	Bactericidal Activity: *B. subtilis*
1.	H	Cl	Ph	Me	113	$C_{17}H_{17}ClN_3O_3PS_2$	+ +	–	+ +
2.	H	Cl	Ph	Et	92	$C_{19}H_{21}ClN_3O_3PS_2$	+	+ +	–
3.	H	Cl	Ph	Pr	115	$C_{21}H_{25}ClN_3O_3PS_2$	–	–	–
4.	H	Cl	Ph	Bu	118	$C_{23}H_{29}ClN_3O_3PS_2$	+	–	–
5.	H	Me	Ph	Me	100	$C_{18}H_{20}N_3O_3PS_2$	+	+ +	–
6.	H	Me	Ph	Et	95	$C_{20}H_{24}N_3O_3PS_2$	+	+ +	+
7.	H	Me	Ph	Pr	85	$C_{22}H_{28}N_3O_3PS_2$	–	+ +	–
8.	H	Me	Ph	Bu	98	$C_{24}H_{32}N_3O_3PS_2$	–	+ +	–
9.	Me	H	Ph	Me	90	$C_{18}H_{20}N_3O_3PS_2$	+	+ +	+
10.	Me	H	Ph	Et	98	$C_{20}H_{24}N_3O_3PS_2$	+	–	–
11.	Me	H	Ph	Pr	169	$C_{22}H_{28}N_3O_3PS_2$	–	+ +	–
12.	Me	H	Ph	Bu	105	$C_{24}H_{32}N_3O_3PS_2$	–	+ +	–
13.	H	Me	4-MeOC$_6$H$_4$	Me	113	$C_{19}H_{22}N_3O_4PS_2$	+ +	+ +	+ +
14.	H	Me	4-MeOC$_6$H$_4$	Pr	168	$C_{23}H_{30}N_3O_4PS_2$	–	+ +	–
15.	H	Me	4-MeOC$_6$H$_4$	Bu	87	$C_{25}H_{34}N_3O_4PS_2$	–	–	–
16.	H	Cl	4-MeOC$_6$H$_4$	Me	146	$C_{18}H_{19}ClN_3O_4PS_2$	–	+ +	–
17.	H	Cl	4-MeOC$_6$H$_4$	Et	188	$C_{20}H_{23}ClN_3O_4PS_2$	–	–	+ +
18.	H	Cl	4-MeOC$_6$H$_4$	Pr	196	$C_{22}H_{27}ClN_3O_4PS_2$	–	–	–
19.	H	Cl	4-MeOC$_6$H$_4$	Bu	199	$C_{24}H_{31}ClN_3O_4PS_2$	–	–	–
20.	Me	H	4-MeOC$_6$H$_4$	Me	91	$C_{19}H_{22}N_3O_4PS_2$	+ +	+ + +	+ +
21.	Me	H	4-MeOC$_6$H$_4$	Et	99	$C_{21}H_{26}N_3O_4PS_2$	+	+ +	+ +

1. Elemental analysis results were within ±0.4% of the calculated values.
2. All the compounds were obtained in 40-60% yield.
3. For antibacterial screening. – = no inhibition, + = 6-8 mm inhibition, + + = 9-5 mm inhibition, + + + = 16-20 mm inhibition.

in presence of anhydrous K_2CO_3 for several hours. The mixture was filtered and concentrated and the solid thus obtained was crystallised from suitable solvent (Table 1).

Biological Data :

Determination of Antibacterial Activity :

The newly synthesised organophosphorous compounds were evaluated for their bactericidal activity against *Staphylococcus aureus*, *Bacillus pumilus* and *Bacillus subtilis* using agar plate diffusion technique[17]. The average inhibition by various compounds has been recorded in Table 1. The results indicate that all the organophosphorous compounds are marginal antibacterial in nature.

Antiacetylcholinesterase Activity

The enzyme activity was assayed essentially according to the method proposed by Diggle *et al*[18] which is a modification of Hestrin's[19] method. The compounds were dissolved in propylene glycol and used at a concentration of 7.4×10^{-5}. A control containing equal volume of propylene glycol was also run in parallel. The inhibition obtained has been recorded in Table 2 along with the I_{50} values of the organophosphates which indicate the concentration required to produce 50% enzyme inhibition.

Table 2—Antiacetylcholinesterase Activity

Sl No.	R_1	R_2	R_3	R	Conc. used	%Inhibition	$I_{50} \times 10^{-5} M$
1.	H	Cl	Ph	Me	7.4×10^{-5}	36.4	10.164
2.	H	Cl	Ph	Pr	7.4×10^{-5}	25.0	13.800
3.	H	Me	Ph	Et	7.4×10^{-5}	18.2	20.329
4.	Me	H	Ph	Me	7.4×10^{-5}	9.1	40.659
5.	Me	H	Ph	Pr	7.4×10^{-5}	9.1	40.659
6	H	Me	4-MeC$_6$H$_4$	Me	7.4×10^{-5}	13.7	27.007
7.	H	Me	4-MeC$_6$H$_4$	Bu	7.4×10^{-5}	13.7	27.007
8.	H	Cl	4-MeOC$_6$H$_4$	Me	7.4×10^{-5}	35.0	10.571
9.	H	Cl	4-MeOC$_6$H$_4$	Pr	7.4×10^{-5}	22.8	16.228
10.	Me	H	4-MeOC$_6$H$_4$	Et	7.4×10^{-5}	18.2	20.329

I_{50} value for Neostigmine, a potent antiacetylcholinesterase inhibitor used as standard in the similar conditions is 1.96×10^{-7}.

Results and Discussion

The acetylcholinesterase activity of O,O-Dialkyl-S-[3-(aryloxymethyl)4-substituted phenyl-1,2,4-triazol-5-yl] dithiophosphates and their I_{50} values are shown in Table 2.

All the compounds exhibit marginal activity except few. The compounds substituted with chloro group in the phenyl ring are better inhibitor of the enzyme. Compound 4 and 5 substituted with methyl group at 3-position are devoid of enzyme inhibitory action. Presence of a methyl group at 4-position did not alter their ability to inhibit acetylcholinesterase. It is seen that as the length of alkyl

chain in phosphorous moiety increases, enzyme inhibition decreases. Compounds having propyl substitution at 'R' are better inhibitors as compared to the ethyl substituted in the phosphorous side chain. Thus in the phosphorous side chain, the order of inhibitory action against acetylcholinesterase is Me>Pr>Et>Bu.

Acknowledgement

The authors express their sincere thanks to the Head, Department of Chemistry, University of Lucknow, Lucknow for providing laboratory facilities. Grateful acknowledgement is made to Mr. H. K. Misra (S.R.F.) and Mr. F. A. Khan (S.R.F.) for their help during bactericidal and AcHE screening. One of us (M.G.) is thankful to the U.P.S.C.S.T. for the award of a J.R.F.

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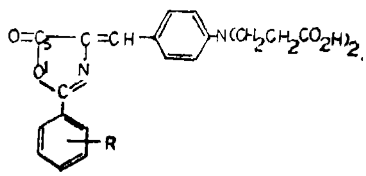
4-NN-*Bis*-2'-Carboxyethylaminobenzaldehyde as Spray Reagent for Acyl Glycines in Paper Chromatography

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Manuscript received 20 February 1979, revised 25 February 1980, accepted 9 July 1980

FORMATION of highly coloured azlactones prompted the use of aromatic aldehydes as reagent for acyl glycines[1-3]. The present note reports the synthesis of 4-NN-*bis*-2'-carboxyethylaminobenzaldehyde (*bis*-CEAB) which on condensation with acyl glycines gave deep coloured 2-substituted phenyl-4-(4'-NN-*bis*-β-carboxyethylaminobenzylidene)-5-oxazolones(I).



(I)

Data concerning the new products are set out in the Table 1.

The use of *bis*-CEAB as spray reagent for acyl glycines has been explored. The sensitivity of *bis*-CEAB is good and the colour produced are generally intense and stable.

Experimental

Synthesis of acyl glycines[4-6] and of oxazolones (I)[1-3] was accomplished as reported in literature. Uncorrected m.ps. are reported.

*4-NN-*Bis*-2'-carboxyethylaminobenzaldehyde* (bis-*CEAB*) :

4-NN-*Bis*-2'-cyanoethylaminobenzaldehyde[7] (10.0 g) and aq. sodium hydroxide (100 ml, 10%) was refluxed for one hr. and the solution was neutralised with conc. sulphuric acid (9.4 ml, density 1.84) when *bis*-CEAB precipitated. It was filtered under suction and recrystallised from water ; m.p. 141° ; yield, 8.2 g. (70.7%). Found : C, 58.3 ; H, 5.98 ; N, 5.56 ; $C_{18}H_{18}O_8N$ requires C, 58.8 ; H, 5.66 and N, 5.28% IR(KBr) shows peaks at 1730 and 1690 cm^{-1} (C=O) and at 1320 cm^{-1} (tert. amino gr.). 2 : 4-Dinitrophenyl hydrazone prepared by usual methods, m.p. 210°.

One per cent solution of *bis*-CEAB in acetic anhydride and fused sodium acetate was found

TABLE 1—PHYSICAL DATA ON 2-SUBSTITUTED PHENYL-4-(4'-NN-Bis-β-CARBOXYETHYLAMINO-BENZYLIDENE)-5-OXAZOLONES(I)

Sl. No.	R	Colour	Colour of the spots	m.p. (°C)	Yield (%)	Mol. Formula	%N Found	%N Calcd.
1.	H	Orange	Orange	226	67.2	$C_{22}H_{20}O_6N_2$	6.81	6.86
2.	Cl(o-)	Bright yellow	Yellow	231	40.9	$C_{22}H_{19}O_6N_2Cl$	6.41	6.38
3.	Cl(p-)	Yellow	Yellow	234	47.7	$C_{22}H_{19}O_6N_2Cl$	6.39	6.33
4.	NO_2(o-)	Orange yellow	Orange yellow	248	35.5	$C_{22}H_{19}O_8N_3$	9.71	9.29
5.	NO_2(p-)	Deep yellow	Deep yellow	256	48.8	$C_{22}H_{19}O_8N_3$	9.79	9.29
6.	Cl(2)NO_2(5)	Yellow	Yellow	238	33.2	$C_{22}H_{18}O_8N_3Cl$	8.41	8.62
7.	Cinnamoyl	Red	Red	240	44.5	$C_{24}H_{22}O_6N_2$	6.84	6.45

effective in producing different colours from yellow to red with acyl glycines on paper.

The colours of the spots have been given in the Table 1.

Acknowledgement

One of the authors (AKS) is grateful to the C.S.I.R., New Delhi for the award of a Junior Research Fellowship.

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Studies on Biologically Active Agents : Synthesis of Variously Substituted N¹-(4-substituted phenoxy acetyl/benzoyl secondary amines)-N²-Substituted Aryl Thioureas as Possible CNS, Anticonvulsant and MAO Inhibitory Agents

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Manuscript received 7 May 1979, revised 22 April 1980, accepted 9 July 1980

SUBSTITUTED thioureas are known to possess pharmacodynamic properties[1-4]. The present communication describes the synthesis of thiourea derivatives by incorporating heterocyclic moiety in the hope that resulting product may have higher biological activities.

These substituted thioureas have been prepared by the condensation of *p*-nitro phenoxy and *p*-nitrobenzoyl chloride with secondary amine. Nitro group was reduced and then reacted with aryl isothiocyanate to obtain the desired product. Some of them were screened, which showed encouraging results.

Experimental

Synthesis of p-*nitrophenoxy acetyl/benzoyl secondary amines :*

They were prepared according to the method of Baker *et al*[5]. Melting points of *p*-nitro phenoxy acetyl and benzoyl dicyclohexylamine were found to be 302° and 200° respectively.

Synthesis of p-amino phenoxy acetyl/benzoyl secondary amines :

They were prepared by the method of Richard and Furst[6]. They are shown in Table 1.

Synthesis of N¹-(4-substituted phenoxy acetyl/benzoyl amines)-N²-substituted aryl thioureas :

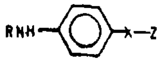
They were prepared according to the method reported by George *et al*[7]. Arylisothiocyanate (0.01 mole) was added to a solution of *p*-aminophenoxyacetyl or *p*-aminobenzoyl secondary amine (0.01 mole) in ethyl alcohol (25 ml). The mixture was heated under reflux for 4 hours. A solid mass was obtained, which was filtered and crystallized from suitable solvents. They are given in Table 1.

Elemental analyses of C, N and H were found within ±0.5% of theoretical and calculated values.

Pharmacological studies :

Toxicity studies : Acute toxicity study was performed with substituted thioureas. These compounds were administered intraperitoneally in albino mice and their approximate LD_{50} were determined by conventional procedure[8].

TABLE 1



Sl. No.	R	m.p. °C	Yield %	LD_{50}*	Anticonvulsant activity Protection %	Mortality %	Monoamine oxidase inhibition %
	Z = Pyrrolidino, X = $OCH_2C(=O)-$						
1.	$C_6H_5NH-C(=O)-$	105	75	681	40	40	40
2.	p-$CH_3C_6H_4NH-C(=O)-$	190	63	681	40	60	70
3.	o-$CH_3C_6H_4NH-C(=O)-$	165	65	–	—	—	—
4.	p-$OCH_3C_6H_4NH-C(=O)-$	200	54	—	—	—	—
5.	p-C_6H_4	185	61	825	40	60	67
6.	α-$C_{10}H_7NHC(=O)-$	175	56	—	—	—	—
7.	H	90	38	—	—	—	—
	Z = Morpholino, X = $-OCH_2C(=O)-$						
8.	p-$ClC_6H_4NHC(=O)-$	165	67	—	—	—	—
9.	p-$BrC_6H_4NH-C(=S)-$	105	57	-	—	—	—
10.	p-$C_{10}H_7NH-C(=S)$	170	59	—	—	—	—
11.	H	79	48	—	—	—	—
	Z = Piperidino, X = $-OCH_2C(=O)-$						
12.	p-$CH_3C_6H_4-NHC(=S)-$	151	61	1000	20	80	—
13.	p-$OCH_3C_6H_4-NHC(=S)$	130	55	—	—	—	—
14.	p-$BrC_6H_4-NH-C(=S)-$	160	55	>1000	60		—
15.	α-$C_{10}H_7NH-C(=S)-$	115	60	—	—	—	—
16.	H	70	50	—	—	—	—
	Z = Dicyclohexylamino, X = $-OCH_2-C(=O)-$						
	p-$CH_3C_6H_4-NHC(=S)-$	202	67	—	—	—	—
18.	p-$ClCH_3C_6H_4-NHC(=S)-$	147-48	40	825	60	40	—
19.	p-$BrC_6H_4NHC(=S)-$	120	58	—	—	—	—
20.	α-$C_{10}H_7NHC(=S)-$	123	33	—	—	—	—
21.	H	240	48	—	—	—	—

(*Table 1 Contd.*)

Sl. No.	R	m.p. °C	Yield %	LD_{50}*	Anticonvulsant activity Protection %	Mortality %	Monoamine oxidase inhibition %
	Z = Piperidino, X = $-C(=O)-$						
22.	$p\text{-}OCH_3C_6H_4NHC(=S)-$	180	58	-4	—	—	—
23.	$p\text{-}ClC_6H_4NH-C(=S)-$	190	50	1000	60	20	62
24.	$p\text{-}BrC_6H_4NH-C(=S)-$	200	48	681	60	40	—
25.	$\alpha\text{-}C_{10}H_7NH-C(=S)-$	185	57	825	20	60	—
26.	H	160	38	—	—	—	—
	Z = Dicyclohexylamino, X = $-C(=O)-$						
27.	$p\text{-}OCH_3C_6H_4NH-C(=S)-$	215	50	—	—	—	—
28.	$p\text{-}ClC_6H_4NH-C(=S)-$	234	64	—	—	—	—
29.	$p\text{-}BrC_6H_4NH-C(=S)$	205	47	825	20	80	—
30.	$\alpha\text{-}C_{10}H_7NH-C(=S)-$	245	48	—	—	—	49
31.	H	242	48	—	—	—	—

In-vivo *effect on Gross behaviour* : It was determined[9] on simple refluxes and behaviour after intraperitoneal administration in albino mice.

Anticonvulsant activity : It was studied[10] against pentylene tetrazole induced seizures on mice.

Monoamine Oxidase activity : Spectrophotometric method[11] was applied for the determination of monoamine oxidase activity of rat brain homogenate using benzylamine as substrate.

Results and Discussion

The approximate LD_{50} value of these compounds ranged from 681 to 1000 mg/kg indicating their low toxicity associated with the compounds and all the compounds of this series had CNS stimulant action.

Anticonvulsant activity was reflected from 20-80%. The presence of *p*-chlorophenyl ring at R position of N^2 and oxymethyl carbonyl at position X exhibited maximum (80%) activity, while methyl and unsubstituted phenyl group at the same position showed low activity (20%). Protection value further diminished from *ortho* to *para* position, due to presence of electron donating group and activity gradually increases due to presence of electron attracting group at the same position.

Monoamine oxidase activity of these compounds was found to be just reverse. The presence of $-OCH_2C(=O)-$ group at X exhibited greater degree of activity and $>C=O$ group reduced the activity at the same position.

Acknowledgement

The authors wish to express their thanks to the Head of Chemistry Department, Lucknow University, Lucknow for providing research facilities. Thanks are also due to Dr. B. N. Dhawan, C.D.R.I., Lucknow for the help in carrying out the screening of compounds.

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On the Dicumyl Peroxide Vulcanisation of Rubber

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Manuscript received 7 May 1977, revised 14 April 1978, accepted 9 July 1980

DICUMYL peroxide (DCP) vulcanisation of rubbers has attracted wide interest in recent years because of its simple chemistry and quantitative results where one carbon to carbon crosslink is formed per molecule of peroxide decomposed[1]. The sulfur vulcanisation of natural rubber (NR) is known to be characterised by a reversion in crosslinking, just after reaching the optimum cure time, and it also produces vulcanisate with poor aging properties. The addition of DCP in sulfur curing system checks both these defects through the inclusion of Carbon-Carbon crosslinks. However, the accelerators, present in the system, may affect adversely[2] on the DCP-NR curing system. In the present paper, the nature and the extent of the effect of the commonly used accelerators on the DCP-NR vulcanisation system has been investigated. The accelerators used are 2-mercaptobenzothiazole (MBT), diphenyl guanidine (DPG) and tetramethyl thiuram disulfide (TMTD).

Experimental

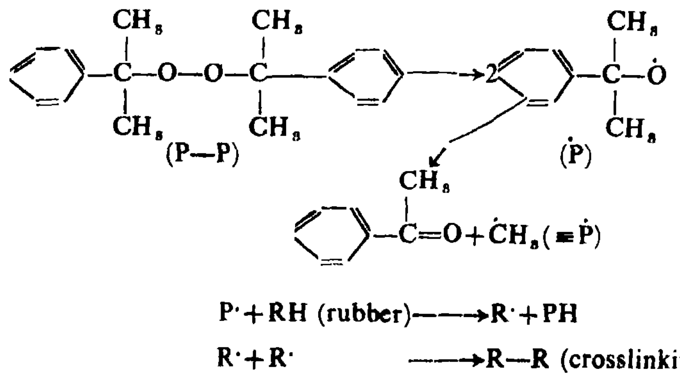
The following sets of compounding formulations were studied. All the formulations given below are in Phr (Parts per hundred of rubber).

NR 100	NR 100	NR 100
DCP 1.0	DCP 1.0	DCP 1.0
MBT, DPG	MBT 1.0	MBT 1.0
or TMTD 0.0, 0.5, 1.0, 1,5, 2.0	DPG 0.0, 0.5, 1.0	TMTD 0.0,0.5, 1.0

Mixing was done on a laboratory size two roll mill at 50° to a constant Mooney viscosity. Each stock was cured in an electrically heated press at 140°±1° and a pressure of 281 psi for various times. Crosslink density of each vulcanisate was determined by equilibrium swelling in benzene as described in the earlier publication[3] of this laboratory.

Results and Discussion

Vulcanisation of natural rubber by dicumyl peroxide has been studied by several workers and the crosslinking reaction has been established beyond doubt to follow a free radical mechanism which can be summarised as follows :



... ... (1)

$$P^{\cdot} + RH \text{ (rubber)} \longrightarrow R^{\cdot} + PH \quad \ldots \ldots (2)$$

$$R^{\cdot} + R^{\cdot} \longrightarrow R{-}R \text{ (crosslinking)} \quad \ldots \ldots (3)$$

$$CH^{\cdot}_3 + CH_3^{\cdot} \longrightarrow C_2H_6 \quad \ldots \ldots (4)$$

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So the effect on crosslink density due to the presence of additives would mean the interaction of the peroxide radicals with those additives.

Effect of Individual Accelerators on DCP Vulcanisation :

Of the three individual accelerators studied, the course of crosslinking by DCP in presence of one representative, namely TMTD, has been shown in Fig. 1. However, the effect of these accelerators on the initial rate of vulcanisation and maximum crosslink density (corresponding to cure time of 150 mins.) of DCP vulcanisation has been summarised in Fig. 2. The salient points observed from these results are as follows :

(i) Each of these accelerators, MBT, DPG and TMTD, inhibits DCP vulcanisation depending on the amount of the accelerator present in the system (Fig. 1).

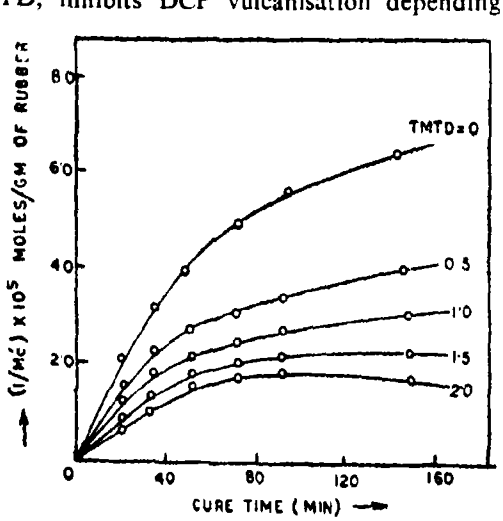


Fig. 1. Variation of crosslink density ($1/M'_c$) in systems containing DCP and TMTD (variable) as a function of cure time.

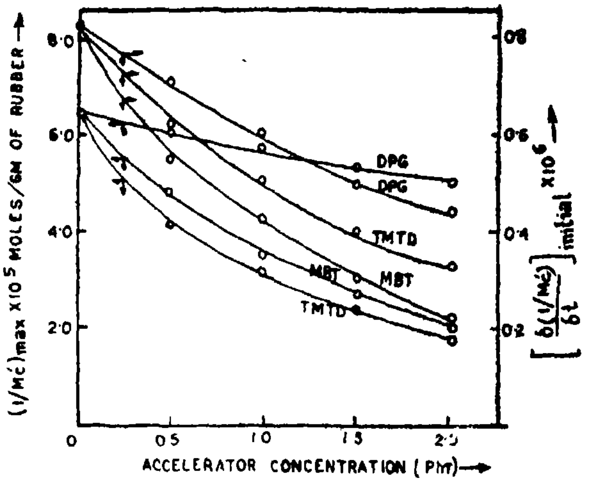
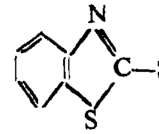


Fig. 2. Change in maximum crosslink density $(1/M'_c)_{max}$ and initial rate of crosslinking on the variable accelerators' concentration.

(ii) The difference in behaviour of these accelerators towards DCP vulcanisation are only in the degree of inhibition at different stages of vulcanisation. Thus, MBT reduces the initial crosslink density more effectively than the others (Fig. 2) whereas the reduction in maximum crosslink density is most with TMTD. And the action of DPG is mild in both the respects (Fig. 2).

All these observations can be explained by reaction schemes where DCP free radicals, responsible for crosslinking, are captured either by accelerator molecules or its decomposition products.

$\dot{P}$ + MSH (MBT) ⟶ PH + M$\dot{S}$ where MSH ≡  ... (5)

$\dot{P}+C_6H_5NH{-}C({=}NH){-}NHC_6H_5 \longrightarrow PH+C_6H_5NH{-}C({=}\dot{N}){-}NHC_6H$ (DPG) ... (6)

$(CH_3)_2NC(:S)SS(S:)CN(CH_3)_2 \longrightarrow 2(CH_3)_2NC(:S)\dot{S}$ (TMTD) (I) or,

$(CH_3)_2N\dot{C}(:S) + (CH_3)_2NC(:S)S\dot{S}$ (II) (III) ... (7)

I, II & III + P· ⟶ Destruction of free radicals ... (8)

Effect of two Accelerators on DCP Vulcanisation :

(a) Action of MBT in combination with DPG : At constant DCP-MBT-NR system, when DPG is gradually added, the crosslink density at all stages of vulcanisation is increased (Fig. 3) than that with only DCP-MBT-NR system. This increasing trend, that depends on the DPG concentration,

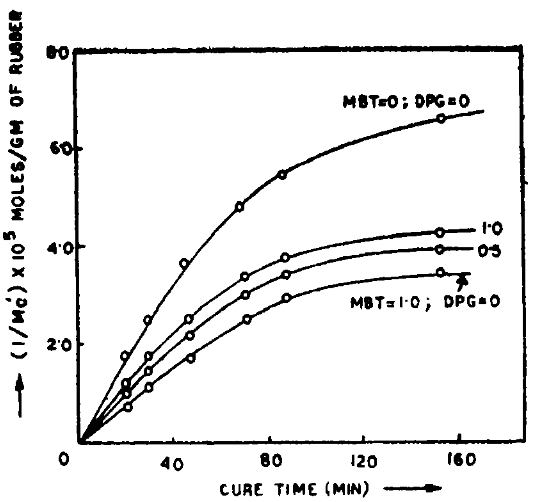
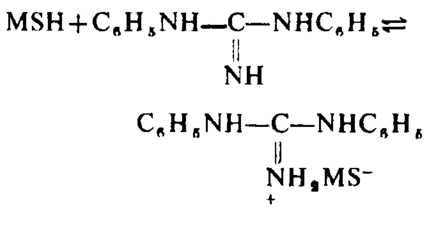


Fig. 3. Variation of crosslink density (I/M'_c) in systems containing DCP, MBT and DPG (variable) as a function of cure time

gets minimised at high concentration of DPG ; this may be due to the limited solubility of this accelerator in rubber. It has already been shown that both the accelerators, when present separately, reduce DCP-crosslinking depending on their concentration and MBT, among them, is the stronger radical scavenger. So these results indicate that DPG, somehow rather, checks the scavenging action of MBT, presumably by reacting initially with MBT as shown below :



... (9)

(b) Action of MBT in combination with TMTD : When TMTD is added in a constant MBT-DCP-NR system, it is observed that with increment in TMTD concentration, the initial crosslink densities (upto 40-50 mins) increase but the final crosslink densities decrease (Fig. 4). This nature of

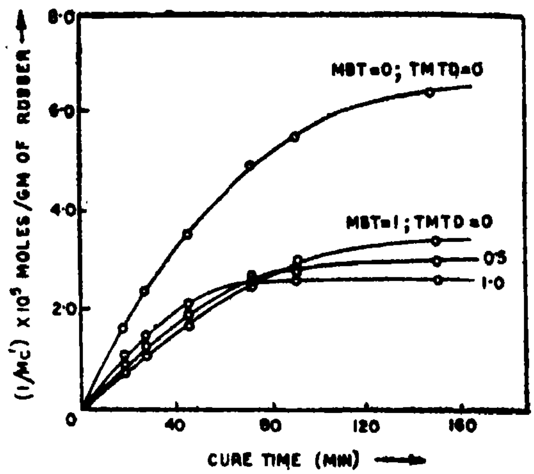
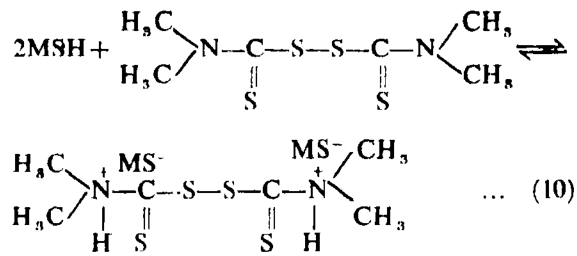


Fig. 4. Variation of crosslink density (I/M'_c) in systems containing DCP, MBT and TMTD (variable) as a function of cure time.

crosslinking at final stage of cure is in contrast with the MBT-DPG-DCP-NR system, where there is a steady increase in crosslink density. The behaviour of MBT-TMTD-DCP-NR can be explained due to the interaction between MBT and TMTD.



... (10)

However, as TMTD is thermally unstable, this complex gets decomposed at the later stages of vulcanisation and generates similar types of free radicals as shown in reaction (7). And these free radicals further inhibit DCP vulcanisation.

From the above study, it can be concluded that DCP vulcanisation of NR is inhibited by the presence of either of MBT, DPG and TMTD. However, the inhibition action is much less when these accelerators are present jointly in a DCP curing system.

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J. Indian Chem. Soc.,
Vol. LVII, September 1980, pp. 956

ADDENDUM*

to the paper entitled

ELECTROPHORETIC MOBILITY... ....FULVIC ACID

by

CHHABI DAS (NEE' DATTA)

J. Ind. Chem. Soc. Vol. **56**, 1141 (1979)

"I regret very much that due to inadvertence and oversight the reference of the work published by Prof. B. N. Ghosh and L. Kundu (J. Ind. Chem. Soc., **47**, 1970, 919) has not been cited in the paper published by me in the November 1979 issue of the Journal of the Indian Chemical Society.

The relationship as mentioned by Dr. (Mrs.) L. Pattrea (nee' Kundu) viz.,

$$\zeta = \text{Const}\ \frac{2RT}{3(P+1)P}\ \ln C$$

was in fact deduced by Prof. B. N. Ghosh and L. Kundu (loc. cit.) and I have given the derivation of the same in my paper as I considered it will be of convenience to the readers."

* The letters received from L. Pattrea (nee' Kundu) (dated May 6, 1980) and Chabbi Das (nee' Datta) (dated June 16, 1980) and relevant research papers were considered by the Publication Committee and it was decided that the above extract of the letter of Dr. (Mrs.) C. Das should be published as an addendum and that further correspondence, if any, in this matter will not be entertained.

Sd/-M. M. Chakrabarty
Hony, Editor
Physical & Industrial Section
Indian Chemical Society

AUTHOR INDEX

J. ... Vol. LVII, October 1980, pp. 957-960

Vanadium(V) Complexes of N-cinnamoyl-N-*o*-methoxy-phenylhydroxylamine and N-cinnamoyl-N-*p*-methyl-phenylhydroxylamine. Its Determination in Alloy Steels and Rock Samples

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Manuscript received 4 October 1978, revised 9 January 1980, accepted 31 March 1980

N-cinnamoyl-N-*o*-methoxyphenylhydroxylamine(I) and N-cinnamoyl-N-*p*-methyl-phenylhydroxylamine (II) form complexes of vanadium(V), bluish violet in color and extractable into chloroform, having λ_{max} at 530 nm and 550 nm with metal to ligand ratio of 1:2 in the acidity range 2-5 (with I) and 1-5*N* HCl (with II). Beer's law is obeyed over 1-14 ppm and 0.4-14 ppm of vanadium with optimum concentration ranges of 2-10 ppm and 1.4-10 ppm for complexes of I and II respectively, the % relative error is 2.70 and 2.72 for the complexes, the molar absorptivities (ϵ) are 6000 and 5900 $l.mol^{-1}cm^{-1}$ while the sensitivities are 0.0085 and 0.0086 $\mu g\ V/cm^2$ respectively.

The extraction constant, K_{ex}, is evaluated from the intercept of the Hiskey-Meloche's plot. A spectrophotometric method based on solvent extraction technique, for the trace analysis of vanadium(V) in presence of diverse ions, in alloy steels and rock samples, has also been described.

EXTENSIVE investigations on the spectrophotometric determination of vanadium(V) have shown that the most sensitive spectrophotometric reagents for the metal are the various disubstituted aromatic hydroxylamine. N-BPHA has been extensively used as a reagent for the solvent extraction and spectrophotometric determination of vanadium[1,2] and for its direct determination in steels[3], alloys, ores[1], blood, urine and plant products and other complex materials[4]. The most sensitive and selective derivatives claimed by various authors are : N-benzoyl-*o*-tolyl-[5] ($\epsilon = 4745$), N-cinnamoyl-N-phenyl[6] ($\epsilon = 6000$), N-*p*-methoxybenzoyl-N-*m*-tolyl[7]-($\epsilon = 5750$), N-2-thenocarbonyl-N-*o*-methoxy-phenyl-[8] ($\epsilon = 7200$) and N-3-styrylacrylcarbonyl-N-phenyl-hydroxylamine[9] ($\epsilon = 7500$).

Present studies have shown that both reagents N-cinnamoyl-N-*o*-methoxyphenyl- (I) and N-cynnamoyl-*p*-methylphenylhydroxylamine(II)[10], are also sensitive and can be deployed for the analysis of alloy steels and rock samples without prior separation of cations present. Both the reagents I and II form bluish violet complexes ($\epsilon = 6000$ with I and 5900 with II) with vanadium(V) in strongly acid medium (2-5*M* HCl) and the species are selectively extracted into chloroform and the color intensity of the complexes are found to remain stable for more than 48 hrs at room temperature. The Beer's law and optimum ranges are 1.0-14 ppm and 0.4-14 ppm, 2-10 ppm and 1.4-10 ppm with both I and II respectively. The composition of the metal : reagent is 1:2 in both the cases. The stepwise stability values calculated, following Leden's and Yatsimirskii's methods, appear more or less of the same order for the complexes. So it can be concluded that the two bidentate chelating groups attach to vanadium simultaneously.

Like other derivatives of hydroxylamines both the reagents I and II also suffer interference from Ti (IV), Mo(VI), W(VI) but with higher tolerence limit for last two ions than other reagents. The interference of Ti(IV) can be removed with fluoride as the masking agent. The reliability of the reagents has been confirmed from their application to the analysis of vanadium containing standard alloy steels and rock samples.

Experimental

Preparation of Reagents : Reagents N-cinnamoyl-N-*o*-methoxyphenylhydroxylamine(I) and N-cinnamoyl-N-*p*-methylphenylhydroxylamine(II) were prepared from *o*-nitroanisole and *p*-nitrotoluene and cinnamoyl chloride according to the procedure described in the literature[11]. The crude reagent, I, a sticky mass, was crystallised from alcohol and acetone. The m.p. of the white needle shaped crystals of reagent I and yellowish needle shaped crystals of reagent II are 100° and 163° respectively. The analysis of the compounds, indicates the formulae of the compound to be $C_{16}H_{15}O_3N$ (I) and $C_{16}H_{15}O_2N$ (II). Standard reagent solutions of desired strength in A.R. chloroform were used. A standard stock solution of vanadium(V) was prepared from A.R. amonium meta vanadate and it was standardised for vanadium content volumetrically[12].

Doubly distilled water was used whenever necessary. Other chemicals used in all spectrophotometric measurements were of A.R. or spectrograde quality.

General Extraction Procedure for Vanadium (V) : An aliquot (1ml of $1.965 \times 10^{-3}M$) of the metal solution was transferred to a separatory funnel (100 ml) and

the acidity of the solution was adjusted using 6*N* HCl solution. Extractions were carried out with equal volume of aqueous to non-aqueous phase (15 ml) by adding required volume of particular reagent, solvent and water. The mixture was then shaken for 5 min and the intense bluish violet chloroform extract was drained out in a 50 ml beaker and dried over anhydrous sodium sulfate. The dried chloroform extract was trasferred to 25 ml calibrated flask. The aqueous layer was further shaken with 5 ml chloroform, extracted and dried as before and then collected in the same flask and finally diluted upto the mark with chloroform. The absorbance of the solution was then measured on a Hilger Uvispek spectrophotometer at 530 nm and at 550 nm (respective λ_{max} of I and II) against solvent as blank.

Evaluation of metal-reagent ratio of the complex : Following the well known distribution method of Hiskey and Meloche[13], and developed further by other workers[14,15], the average number of ligands bound to the vanadyl ion was established to be 2 and the log $K_{f,n}$ computed by the graphical method.

Results and Discussion

Absorption Spectrum : The absorption spectra of the colored system in chloroform obtained with reagents I and II was measured in the wavelength region 400 nm to 620 nm against chloroform as blank. The spectral curves show that V(V) complex with reagent I absorb maximum at 530 nm and with reagent II at 550 nm where the reagents possess no absorption.

Effect of acidity : The intensity of the coloredV(V) complexes was found to be maximum at the overall acid concentration of 2-5*N* and 1-5*N* with reagents I and II respectively. Increase of acid concentration results in the decrease of color intensity.

Effect of reagent concentration : 5.0 ml of 0.5% (w/v) solution of reagent I and of 0.1% (w/v) solution of reagent II in chloroform is sufficient for maximum color development of V(V) (4 ppm) complex at the particular acidity. Addition of more reagent had no effect.

Calibration curve, optimum range and photometric error of the complexes : The colored systems obeyed Beer's law from 1-14 ppm and 0.4-14 ppm at 4*N* and 2*N* HCl with reagents I and II respectively at λ_{max}.

To evaluate optimum range and analytical accuracy, Ringbom's[16] curves were drawn by plotting % absorbance as ordinate against log concentration of metal as abscissa. The optimum concentration range with the highest accuracy for V(V)-reagent I complex is from 2-10 ppm and for reagent II complex is from 1.4-10 ppm.

The percent relative error per 1% absolute photometric error was calculated according to the Ayres'[17] equation and was found to be 2.70 and 2.72 for I and II systems respectively.

Molar absorptivity and sensitivity : The molar absorptivity values for the complexes were calculated from Beer's law data and are found to be 6000 and 5900 $l.mol^{-1}\ cm^{-1}$ for V(V) complexes with I and II. Corresponding to the Sandell[18] sensitivities of 0.00854 $\mu g\ V/cm^2$ and 0.00862 $\mu g\ V/cm^2$ repectively.

Effect of diverse ions : To study the effect due to other ions, solutions with varying concentrations of different diverse ions were prepared with reagents (I and II as the case may be) following the general procedure described earlier and 4 ppm of vanadium (V). It was observed that it suffered interferences mainly from Ti(IV), Mo(VI), W(VI), Nb(V) and Zr(IV) but with higher tolerance limits. Interference due to Ti(IV) can be avoided using NaF in excess as a masking agent. Interference due to Mo(VI) can be removed by ethyl xanthate-extraction[19].

Tolerance limits of the ions in ppm are shown within brackets. Citrate (1000), oxalate (1000), tartrate (500), F^- (1000), EDTA (1000), PO_4^{-3} (1000), acetate (1000), Al^{+3} (200), Be^{+2} (200), Mg^{+2} (200), Ba^{+2} (200), Zn^{+2} (200), Sr^{+2} (200), Pb^{+2} (200), Hg^{+2} (150), Cd^{+2} (200), As^{+3} (150), Fe^{+3} (200), Co^{+2} (200), Ni^{+2} (200), Cr^{+3} (200), Mn^{+2} (200), In^{+3} (200), UO_2^{+2} (200), Ti^{+4} (S.I)*, MoO_4^{-2} (50), W^{+6} (80), Th^{+4} (200), Nb^{+5}(20), Ta^{+5} (20), Zr^{+4} (60).

Procedure for the analysis of High Speed Steel(BAS 64b-containing 1.99% V) : The sample (0.6 g) was dissolved in dilute (1:4) sulphuric acid and it was evaporated to a syrupy mass on a hot plate. The process was repeated twice with 5 ml of the acid each time. Finally, the solution was treated with an excess (5 ml) of concentrated sulphuric acid followed by 2 ml of concentrated nitric acid. The solution was evaporated slowly in a fuming chamber till the evolution of free SO_3 fumes. It was then cooled and diluted to about 50 ml with doubly distilled water. The solution was warmed to dissolve any undissolved solid matter and filtered through a Whatman No. 42 filter paper. The residue was washed several times with hot water. The filtrate and washings were collected and the volume made upto 250 ml.

An aliquot of the above solution was oxidised in hot by the addition of dilute potassium permanganate solution. The vanadium content was determined following the general extraction procedure. The percentage of vanadium in the sample was found to be 1.98% with I and 1.97% with II.

Procedure for Rock Analysis : *Determination of vanadium in Ilmenite and other different samples* : Transfer finely powdered sample of ilmenite (Hornbendite rock, contains 0.1% vanadium)(1.0 g) in a silica crucible. Fuse with potassium bisulphate (5.0 g) for first decomposition, continue after the addition of

*S. I.—seriously interferes.

another 5.0 g potassium bisulphate till the sample completely decomposed. Cool the melt and leach with (1 + 9) sulphuric acid in 250 ml beaker and this is heated nearly to boiling. Neutralise the solution of the decomposed sample, 'and concentrate to a small volume. Excess titaniam and iron in the samples are reduced by precipitating as hydroxides by treating with dilute ammonia (1 : 1). Filter into another beaker by careful washing with minimum quantity of hot water. Any vanadium adsorbed on the hydroxides is recovered by reprecipitation. The two filtrates are combined and concentrated to about 50 ml by evaporation. Acidify to litmus with dilute sulphuric acid and make up the volume of the solution to 100 ml in volumetric flask.

Transfer 10 ml of aliquot of this solution to a 100 ml beaker. Oxidise vanadium in hot by adding 0.1% potassium permanganate solution until the pink color persists. Determine the vanadium content in the solution following the general procedure by adding excess ammonium fluoride (~0.2 g) at 4*N* HCl. Then calculate the percentage of vanadium in the sample. The results of a few analysed samples using reagent are given in table 1.

TABLE 1—RESULTS ON ANALYSED SAMPLES

Sample	Percentage of Vanadium Found	Reported
1. *Ilmenite (Hornblendite rock, Kavur Anchal, Tamilnadu, India)	0.098	0.1
2. Ilmenite (collected from Indian Oxygen Ltd., Calcutta)	0.124	0.130
3. Ilmenite*, IGS-31 (London)	0.065	0.062
4. Magnetite* (Titaniferrous Magnetite)-TM, GSI, Calcutta.	1.02	1.05

*Collected from G.S.I., Calcutta.

Composition of the complexes : The composition of the complexes with reagents I and II have been found to be 1:2 by applying Job's[20,21] and molar ratio[22] methods. These are further verified from the graphical plot of log (Distribution coefficient) vs. log $[\text{reagent}]_{org}$ − *p*H of Hiskey-Meloche's method[13-15].

Evaluation of Stability and Equilibrium Extraction constants : The stepwise stability constants were calculated following the extended Yatsimirskii's[23] and Leden's[24,25] methods.

The degree of dissociation, α and overall stability constants K_{ov}, were further verified by Harvey and Manning's method[26]. The equilibrium extraction constants, K_{ex} for the complexes were obtained from extrapolation of distribution method. The different values of stability constants along with equilibrium extraction constants are given in Table 2.

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TABLE 2—STEPWISE AND OVERALL STABILITY AND EXTRACTION CONSTANTS FOR V(V)-REAGENTS (I AND II) COMPLEX SYSTEMS AT 27°C

	Leden's Method			Yatsimirskii's Method			Harvey-Manning's Method	Extraction constant (Hiskey-Meloche's method)
	log K_1	log K_2	log K	log K_1	log K_2	log K	log K	log K_{ex}
1. V(V)−I system	4.32	4.28	8.60	4.63	4.14	8.77	8.93	8.80
2. V(V)−II system	3.81	3.77	7.58	3.90	3.53	7.43	7.94	7.60

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 961-964

The Effect of 'R' Group in *Bis* (N-R, Salim) Nickel (II) on the Dehalogenation of Chloroform

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Manuscript received 18 June 1979, accepted 26 July 1980

The study of the effect of 'R' group on the dehalogenation of chloroform prompted by the ligand substitution reaction system, consisting of *bis* (N-R, salim) nickel (II) (with $R=H, CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9, s\text{-}C_4H_9, t\text{-}C_4H_9$) and N,N,N',N'-tetramethylethylenediamine has been carried out. The kinetics study has been followed by the measurement of rate of chloride release at five different temperatures. It has been observed that both, the basicity and geometrical characteristics of the R group control the kinetics of dehalogenation. A relationship between Taft substituent parameter of the R group and energy of activation has been observed. The deviation observed from this relation (R=H) has been attributed to the geometrical factors. The nature of the proposed intermediate has been substantiated by showing a correlation between the energy of activation and the downfield chemical shift of the methine proton. The data of activation entropy and enthalpy changes follow the isokinetic relationship, indicating the importance of the structural factors of the Schiff base complexes in the dehalogenation reaction.

It has been reported[1] that the amine exchange reaction between *bis* (N-n-butyl, salim) nickel(II) and diamines in chloroform involves a dehalogenation reaction of chloroform. An activated complex containing nickel(II) with seven coordination number has been proposed. This work will have to be substantiated by determining the kinetics data using *bis* (N-R, salim) nickel (II) with R having different basicity and geometrical configuration. The present work reports such kinetics data using *bis* (N-R, salim) nickel (II) with $R=H$, CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$.

Experimental

The conventional procedures[2] were used for synthesis of Schiff base complexes of nickel(II), *bis* (N-R, salim) nickel (II) (with $R=H$, CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$). The complexes were tested for purity by determining i.r. spectra, elemental analysis and melting point[3,4]. The i.r. spectra were determined using nujol and hexachlorobutadiene mulls on Beckman IR-4 spectrophotometer. The e.m.f. measurements were done on Radiometer PHM 4a *p*H meter.

For the kinetics measurements, a three-necked flask (300 ml) was equipped with a reflux condensor, glass electrode and silver-silver chloride electrode. The experimental solution (200 ml) was poured into this flask and maintained at a specific temperature ($\pm 0.1°$) by using the oil thermostat. The experimental solution was prepared in a 250 ml volumetric flask by mixing 120 ml of chloroform solution of *bis* (N-R, salim) nickel (II) (0.250×10^{-3} *M*) and 120 ml of N,N,N',N'-tetramethylethylenediamine (8.58×10^{-3}*M*) in methanol, and adjusting the total volume to 250 ml using methanol-chloroform mixture (1:1 V/V).

The pseudo-first order rate constants, k, were calculated by using the equation, $k=2.303$ m ; here m is the slope of the linear plot of $-\log(V_\infty - V_t)$ vs time, t (in seconds) ; V_t and V_∞ are the potentials across the electrodes of the experimental solution at time t, and at the end of the reaction. The thermodynamic constants of the reaction—the energy of activation and the enthalpy and entropy of activation—were calculated by using the usual equations.

Results and Discussion

The results are summarized in Table 1.

In the dehalogenation of chloroform by a Schiff base complex, *bis* (N-R, salim) nickel (II), the chelate exchange reaction is the rate determining step. (Eqn. 1). It is obvious that, the basicity of R group and the geometry of the original complex will affect the rate of reaction. In solution, the complexes, *bis* (N-R, salim) nickel (II) are square planar with $R=H$, and are compressed tetrahedral with $R=n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $s\text{-}C_4H_9$ and $t\text{-}C_4H_9$[5] ; with $R=CH_3$ and C_2H_5 there is an equilibrium between the square planar and tetrahedral configurations[6]. These changes in the geometry are related both to the size and the electronic effect of the R group.

The geometrical changes in the complex molecules, due to these factors will change the nature of hybrid atomic orbitals on oxygen, participating in metal-oxygen coordination[7]. It is therefore logical to expect a correlation between the activation energy of the dehalogenation reaction under consideration and the electronic properties of the substituent R, after giving due considerations to the geometrical factors of group R.

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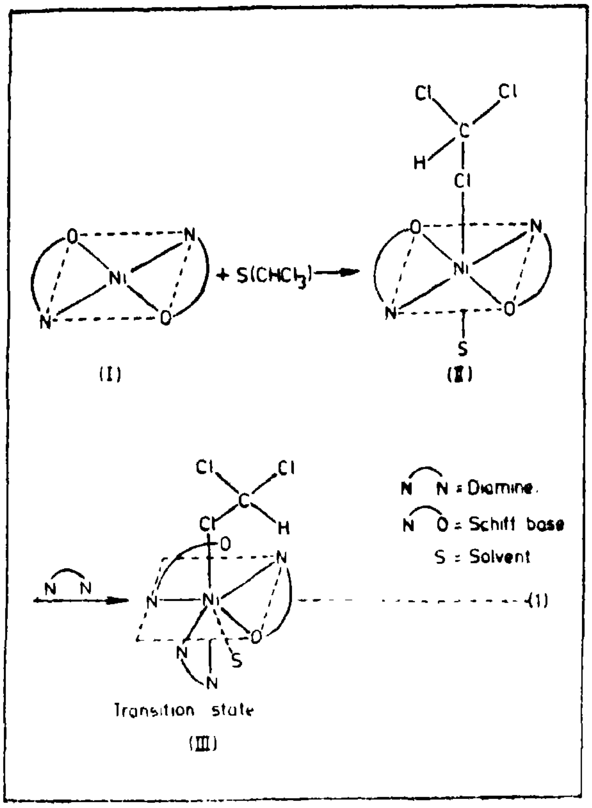
TABLE 1—KINETICS OF DEHALOGENATION OF CHLOROFORM

Complex*	Temp., °C	Pseudo-first order rate constant (sec^{-1}) $k \times 10^4$	Energy of activation (kcal/mole)	Entropy of activation (e.u.)	Enthalpy of activation (kcal/mole)	Chemical shift δCH (ppm***)
1. *Bis*(N-ter-butyl, salim) nickel (II) (−0.30)	60 63 67 71 75	0.90 1.40 2.10 3.00 3.25	18.4±0.1	−23.8	17.7±0.1	8.21
2. *Bis*(N-Sec-butyl, salim) nickel (II) (−0.21)	60 63 67 71 75	1.05 1.60 2.25 3.20 3.40	17.5±0.1	−26.7	16.8±0.1	8.20
3. *Bis*(N-n-butyl, salim) nickel (II) (−0.13)	60 63 67 71 75	1.20 1.87 2.40 3.50 3.65	16.1±0.1 (17.2±0.6)**	−31.0 (−27)**	15.4±0.1 (16.5±0.6)**	8.15
4. *Bis*(N-n-propyl, salim) nickel (II) (−0.115)	60 63 67 71 75	1.80 2.10 2.70 3.60 4.10	13.8±0.1	−37	13.1±0.1	8.16
5. *Bis*(N-ethyl, salim) nickel (II) (−0.110)	60 63 67 71 75	2.10 2.60 3.00 3.70 4.20	10.0±0.1	−47.9	9.3±0.1	8.06
6. *Bis*(N-methyl, salim) nickel (II) (0.000)	60 63 67 71 75	2.60 2.80 3.40 3.84 4.45	6.9±0.1	−56.9	6.2±0.1	8.01
7. *Bis*(N-H, salim) nickel (II) (+0.490)	60 63 67 71 75	2.80 3.30 3.60 4.00 4.50	5.9±0.1	−59.7	5.2±0.1	

* The quantities given in brackets in the first column are the Taft substituent parameters of the R group.

** D. F. Martin, *J. Inorg. Nuclear Chem.*, 1975, 37, 1941.

*** G. C. Percy and D. A. Thorton, *J. Inorg. Nuclear Chem.*, 1972, 34, 3371.



(Eqn. 1.)

A graphical representation between the energy of activation of dehalogenation reaction and Taft substituent parameter[8] which is the measure of the electronic polarization effect of the substituent, indicates that the point corresponding to R = H has a large deviation from this representation. If the basicity of the R group was the only factor deciding the kinetic aspects of the dehalogenation reaction, a uniform correlation between Taft substituent parameter and energy of activation would have been obtained. The experimental observations indicate that the geometrical factors are of equal importance. It may be suggested here that Taft substituent parameters depend on geometry.

In tetrahedral geometry, the hybridization of the atomic orbitals on oxygen will be of sp^3 type which will have better overlap with the metal orbitals. The energy of activation for the dehalogenation reaction using tetrahedral complexes will therefore be higher than that using the square planar complexes.

The change in electron density on nitrogen and oxygen of a Schiff base due to the hyperconjugative effect of R group will be reflected on the downfield chemical shift of the methine proton[9]. As we have seen above, the electron density at oxygen and nitrogen controls also the activation energy of dehalogenation reaction. The favourable hyperconjugative effect of the R group will increase the electron density on coordinating nitrogen and oxygen, and will deshield the methine proton. A higher energy of activation is, therefore, expected for a compound having a higher value of the methine proton chemical shift. The experimental observations are according to this prediction (Fig. 2).

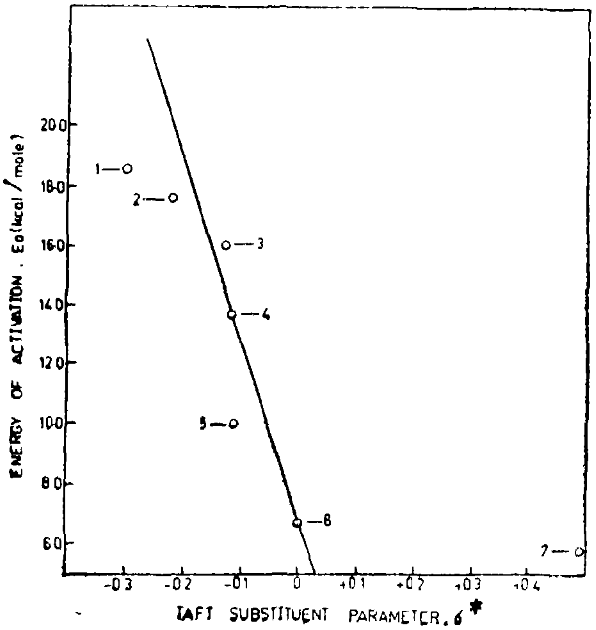


Fig. 1. Relationship between energy of activation and Taft substituent parameter for the ligand substitution reaction of *bis* (N-R, Salim) nickel (II).

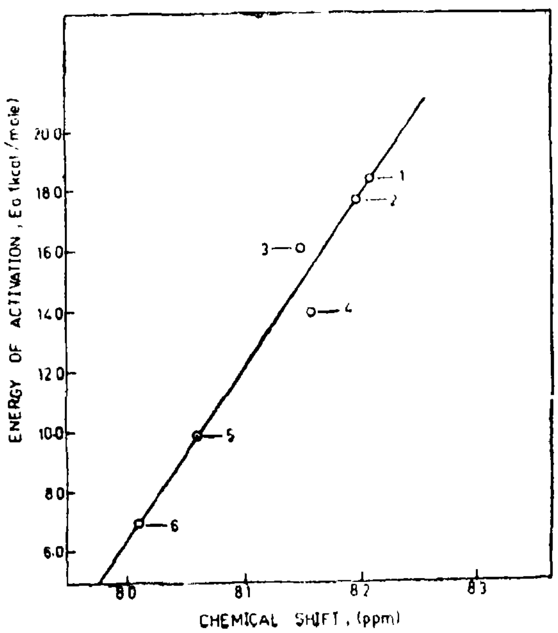


Fig. 2. Relationship between downfield chemical shift of the methine proton (in $CDCl_3$ relative to TMS) and energy of activation for the ligand substitution reaction of *bis* (N-R, salim) nickel (II).

It is interesting that an excellent isokinetic relationship[10,11] has been observed between the activation

entropy change ($\Delta S^{\neq}$) and activation enthalpy change ($\Delta H^{\neq}$) of the dehalogenation reaction (*Fig. 3*). This observation suggests that both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are decidely dependent on the structure of the reaction intermediate[12]. The effect of changing R on $\Delta H^{\neq}$ is proportional to the effect on $\Delta S^{\neq}$.

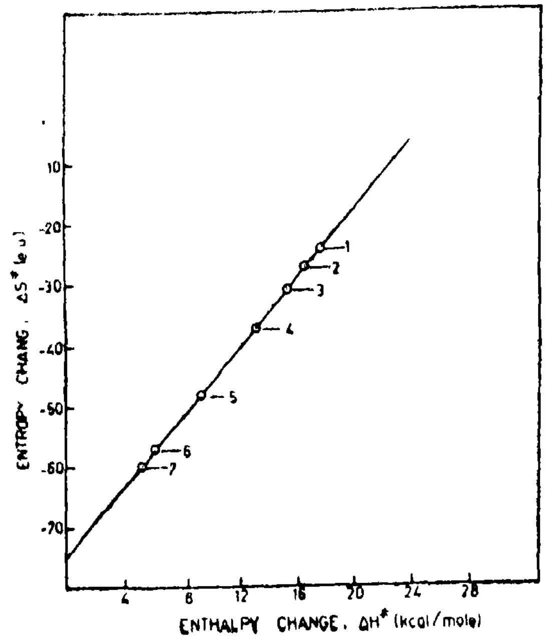


Fig. 3. Isokinetic relationship for the ligand substitution reaction of *bis* (N-R, salim) nickel (II).

For all the systems studied in the present work $\Delta S^{\neq}$ is negative. This supports the proposed activated complex which takes up one more ligand from the medium. The solvation also contributes to the negative change in entropy. It seems that the entropy change depends on the R group ; lower the value of Taft substituent parameter lower is the value of entropy change. It has been also observed that a reaction having higher activation energy has less negative entropy change.

To summarise, the present kinetics study substantiates the mechanism for the dehalogenation reaction of chloroform involving the addition intermediate. The magnitude of the energy of activation depends on the contribution of the R group to the hyperconjugative effect and the geometry of the ground state of metal complexes in solution.

Acknowledgement

Our thanks are due to Council of Scientific and Industrial Research, New Delhi, India, for Junior Research Fellowship (C.T.N.). Our thanks are also due to Prof. V. K. Phansalkar, Head of the Department of Chemistry, University of Poona, Pune-411 007, for giving the necessary facilities during the work. We also thank Dr. Mrs. B. R. Kundalkar for her help during a part of the work.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 965-966

Studies on Fe(II) and Cd(II) Chelates of L-Lysine Monohydrochloride

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Manuscript received 12 September 1979, revised 26 May 1980, accepted 26 July 1980

L-Lysine monohydrochloride has been investigated as a ligand and it has been found that it forms 1:1 chelates with Cd(II) and Fe(II). The two chelates have been isolated and their formulas determined on the basis of chemical analysis. The I.R. data and magnetic measurements have been used to assign structure to the chelates.

THE survey of literature reveals that L-lysine monohydrochloride as a ligand has not been systematically studied. Kaczmarek and Marion[1] have found that lysine forms complexes with nickel in the molar ratio of 1:1 and 2:1. The formation of double salt of optically active L-lysine monohydrochloride with lithium chloride is reported[2]. Preliminary studies on the complexes of lysine with cobalt[3], molybdenum[4], copper[5] and chromium[6] have also been carried out. The present communication reports on the isolation and characterization of Fe(II) and Cd(II) chelates of L-lysine monohydrochloride.

Experimental

Cadmium sulphate, ferrous ammonium sulphate (B.D.H., AnalaR) and L-lysine monohydrochloride (Switzerland, Fluka) were used without further purification. Their solutions were prepared in water distilled over alkaline potassium permanganet.

All conductance measurements were made with a conductivity meter type LBR/B (W.T.W., German make) and pH measurements on Beckman pH-meter standardised with phthalate and borax buffer. Magnetic measurements of chelates were done at room temperature ($25\pm1°$) on Gouy's magnetic balance.

Isolation of chelates studied :

10 ml of aqueous solution (0.1 M) of the ligand was slowly added to a beaker containing 10 ml of aqueous solutions (0.1 M) of ferrous ammonium sulphate and cadmium sulphate. The pH of the resulting mixture was raised to about 8.0 by the addition of NaOH solution drop by drop. The mixture was warmed up, allowed to stand overnight and then concentrated over a water bath. On cooling the complex precipitated. The complexes were filtered, washed with ice cold water, recrystallized from distilled water and finally dried in vacuum desiccator over anhydrous calcium chloride.

Results and Discussion

The composition of both the chelates was established using Job's method of continuous variation[7] and also molar ratio[8] method. For Job's method, equimolar solutions (0.002 M) of the metal and the ligand were mixed and their ratio was varied from 1:9 to 9:1. The conductance measurements of the resulting solutions revealed that both the metals form complexes with the ligand in the molar ratio of 1:1.

The molecular formulae assigned to complexes on the basis of analytical results as given below also show that metal to ligand ratio is 1:1.

(*i*) *Cd(II) complex* (*Cadmium lysinato chloride*) :

	C	H	N	Cl	Cd
Found	16.44	6.51	5.59	7.90	25.22 percent
Calcd. for $(CdC_6H_{13}N_2O_2)Cl.8H_2O$	16.54	6.65	6.42	8.1	25.68 percent

(*ii*) *Fe(II) Chelate* :

	C	H	N	Cl	Fe
Found	19.52	7.00	7.62	9.52	15.00 percent
Calcd. for $(FeC_6H_{13}N_2O_2)Cl.7H_2O$	19.88	7.45	7.74	9.80	15.46 percent

I.R. and magnetic data :

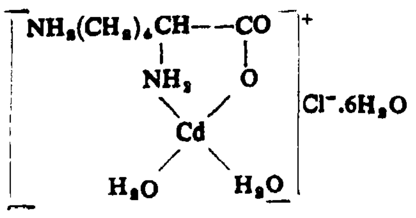
The following principal bands were obtained in the I.R. spectra of the ligand and its chelates

	$\nu(NH_3^+Cl)$	$\nu asym(CO\bar{O})$	$\nu sym(CO\bar{O})$
Ligand	2100 cm^{-1}	1560 cm^{-1}	1390 cm^{-1}
Cd-Chelate	—	1590 cm^{-1}	1360 cm^{-1}
Fe-Chelate	—	1610 cm^{-1}	1400 cm^{-1}

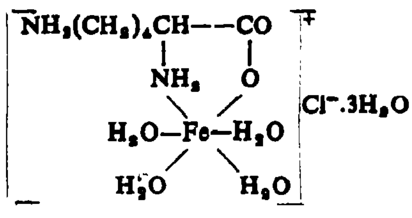
The band at 2100 cm^{-1} in the ligand and assigned to -NH_3^+Cl group[9] disappears in chelates due to the fact that the chelates were isolated at *p*H of about 8.0 and, therefore the -NH_3^+ group got deprotonated. It is well known that amino acids[10] exist as dipolar (Z wittor ions) in crystalline state and therefore two relevent I.R. bands of amino acids from coordination point of view are antisymmetric and symmetric stretching frequency of carboxyl group. Of these two the antisymmetric $CO\bar{O}$ stretching frequency is much more sensitive[11] than the symmetric one and its value in a complex is a function of the mass, radius, charge and electronegativity of the metal. Thus any shift in ν_{asym} ($CO\bar{O}$) is taken as a sufficient measure of the carboxylate group coordinating to the metal. It is seen from the table already given that ν_{asym} ($CO\bar{O}$) in Cd(II) and Fe(II) chelates is significantly increased to higher value indicating coordination of the carboxyl group to the metal. The increase in frequency is due to formation of M-O bond[10-12] which lengthens one C-O band, making thereby both the oxygen atoms non-equivalent. Thus by M-O bond formation the $\nu_{assymmetry}$ of $CO\bar{O}$ group is increased and thereby ν_{asym} ($CO\bar{O}$) is also increased. It is therefore, expected that more the covalent character of M-O band, more would shift in ν_{asym} to higher frequency. Our results do indicate that ν_{asym} ($CO\bar{O}$) for Fe(II) chelate is higher than that of Cd-chelate. This is due to the fact that Fe^{2+} being smaller in size forms a bond with oxygen which is of much greater covalent character.

The I.R. spectra of the ligand also has a broad band in the region 2800–3400 cm^{-1} evidently due to O-H and N-H stretches and it almost remains intact in the spectra of chelates. On the basis of above I.R. evidence the chelates may be assigned following structures.

The molar conductance of the chelates were found to be 75 and 50 ohm^{-1} cm^{-1} for Cd(II) and Fe(II)-chelates which confirms their uni-univalent type electrolytic structure. The presence of chloride ions outside the coordination sphere was further confirmed by silver nitrate test.



Cadmium lysinatochloride



Iron Lysinatochloride

Both the Fe(II) and Cd(II) chelates were found to be diamagnetic and had effective magnetic moment values of 0.50 and 0.57 B.M. indicating the absence of unpaired electron. The absence of unpaired electron in case of Fe(II) chelate indicates that Fe(II) forms inner orbital low spin complex through d^2sp^3 hybridisation and its oxidation state remains +2 during chelation.

Acknowledgement

The authors are grateful to Dr. I.B. Gulati and Dr. R.K. Srivastava, I.I.P., Dehradun for their kind help rendered to us in various analysis, to Dr. W.U. Malik of Roorkee University for providing magnetic measurements facility and to Principal N.S. Varma and Dr. P.K. Sharma, D.A.V. College, Dehradun for their encouragement in the work.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 967-970

Effects of Substituents on the Intramolecular Hydrogen Bond in 8-Quinolinol-N-Oxides**

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Manuscript received 25 September 1978, revised 8 June 1979, accepted 31 March 1980

I. R. spectral and deuteration studies on 8-quinolinol-N-oxides and its 5-nitro-, 5-nitroso-, 5-amino-, 5-phenylazo-, 5, 7-dibromo- and 5, 7-diiodo-derivatives in solid and in solution state confirm the presence of a strong intramolecular unsymmetrical hydrogen bond involving the hydroxyl hydrogen atom and the N-oxide oxygen atom. The structure of the complex absorption pattern in the region 2850 cm.$^{-1}$ – 1800 cm^{-1} is explained in terms of Fermi resonance interaction between the ν_{OH} of O–H...O and the overtone and combination bands of ($\delta_{OH}+\nu_{C-O}$) and other fundamental vibrations of the molecule. The absence of any significant absorptions in the ν_{OH} region in the spectra of 5,7-dichloro- and 5,7-dinitro-derivatives coupled with strong and broad absorption in 1500 cm.$^{-1}$ – 600 cm.$^{-1}$ region is perhaps due to the presence of very short hydrogen bonds in these compounds.

IN recent years there has been considerable discussion of very short (less than 2.5 Å) hydrogen bonds (OH...O) between oxygen atoms[1-4]. Compounds with extremly short H-bonds are of interest since they show unusual spectral features and might include instances of symmetrical H-bonds. During our studies[5] on "8-quinolinol-N-oxide and some of their metal chelates", we had noticed very complex hydroxyl absorption pattern over a wide range 2850 cm^{-1} – 1850 cm^{-1} in the I.R. spectrum of 8-quinolinol-N-oxide. The series of medium strong bands, on deuteration, shifted and a simplified pattern with three prominent absorptions was observed. It is considered of interest to investigate in detail the origin of this complex absorption and also to study the effect of substituents on the strong intramolecular hydrogen bond present in these N-oxides. Solid and solution I.R. spectra of several 5-substituted and 5,7-di substituted-8-quinolinol-N-oxides and their duetero analogues have been recorded and the results of our studies are presented in this paper.

Experimental

8-Quinolinol-N-oxide and its 5-and 5,7-disubstituted derivatives were prepared by the reported methods[6-9] and were purified by repeated recrystallizations. Their purity was checked by elemental analysis. All the solvents were purified by standard methods. The deutero analogues were prepared by either refluxing with D_2O (99.8%, Atomic Energy Commission, Bombay) (in the case of 8-HOQNO) or with acetonitrile and D_2O under N_2 atmosphere, followed by evaporation of the solvent under reduced pressure. I.R. spectra were recorded on Perkin Elmer 221 infrared spectrophotometer with sodium chloride prism grating interchange (spectral slit width 1.5–2 cm^{-1} in the region 3000-1800 cm^{-1}), using Nujol or hexachlorobutadiene mulls in the solid state or wherever possible, in solvents such as CCl_4 (concentration ranges ~1×10^{-4}m).

Results and Discussion

The spectra of 8-quinolinol-N-oxide in solid as well as in solution show multiple medium strong absorption bands over a wide range 2850 cm^{-1}-1800 cm^{-1}. In solution spectra the band profiles are unaffected by dilution. These bands are shifted and simplified on deuteration. In 5-nitro, 5-nitroso-, 5-amino-, 5-phenylazo-, 5,7-dibromo- and in 5,7-diiodo-8-quinolinol-N-oxides the absorption pattern is essentially similar. All the spectra of substituted-8-quinolinol-N-oxides except the 5, 7-dichloro- and 5, 7-dinitro-derivatives exhibit definite pattern of absorption in three main regions at ca.2850 cm^{-1}, ca.2400 cm^{-1} and at ca.1800 cm^{-1}. In some cases (5-NO_2-, 5-NO-, 5-N=NC_6H_5- and 5-NH_2-derivatives), they have contours rather broad and or weak and in others (5,7-dibromo- and 5,7-diiodo-), they are split into several submaxima (Figs. 3 and 4). However, the absorption (ν_{OH} regions) is irregularly increasing extending to ca.1800 cm^{-1}. The bands observed in the spectra, in general, at ca.2800 cm^{-1} moved on deuteration to ca.2400 cm^{-1} and those at ca.2400 cm^{-1} moved to ca.1800 cm^{-1}. The shift of the bands at ca.1800 cm^{-1}, however, could not be located. One common feature found in the deutero analogues of these substituted-N-oxides is the partial changes in the shape and intensity of absorption bands at ca.1600-1550 cm^{-1}. The other coupled vibrations, $\delta_{OH}+\nu_{(C-O)}$ and the out of plane deformation mode γ_{OH} also moved on deuteration. The observed absorption features in the region

**Communication No.: 2299 from the N. C. L., Poona-8.

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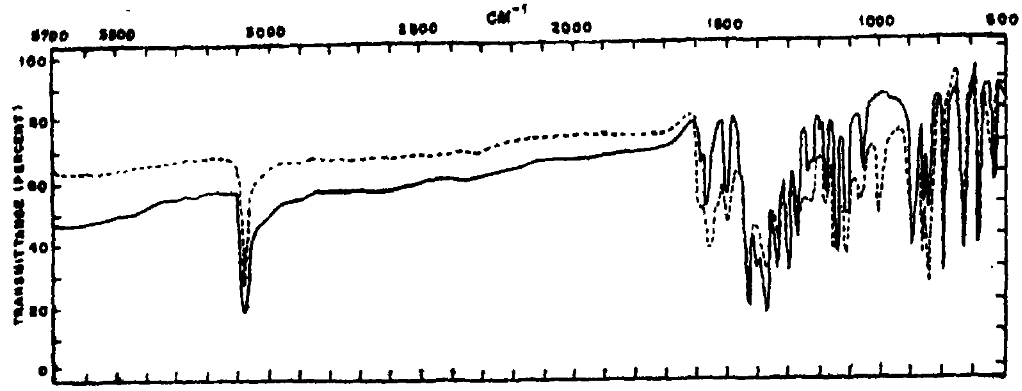


Fig. 1. —Infrared spectrum of 5, 7-dichloro-8-quinolinol-N-oxide solid (3700 cm^{-1} to 600 cm^{-1})

...The deuterated analogue.

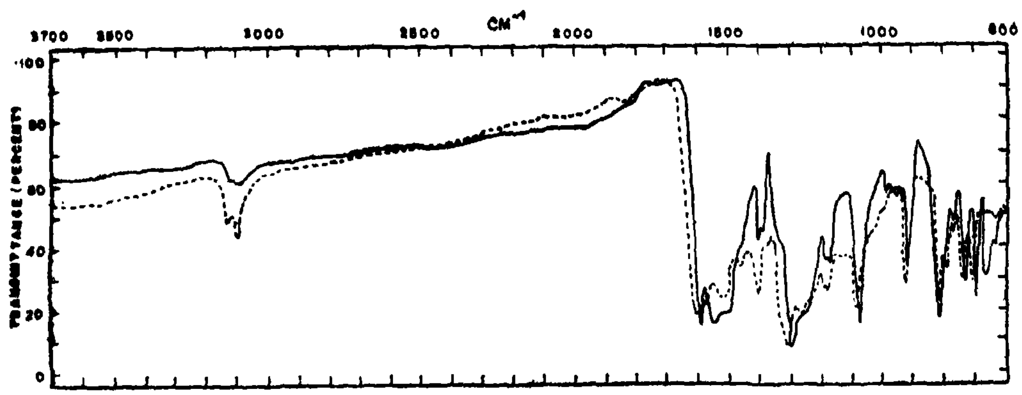


Fig. 2. —Infrared spectrum of 5, 7-dinitro-8-quinolinol-N-oxide solid (3700 cm^{-1} to 600 cm^{-1})

...The deuterated analogue.

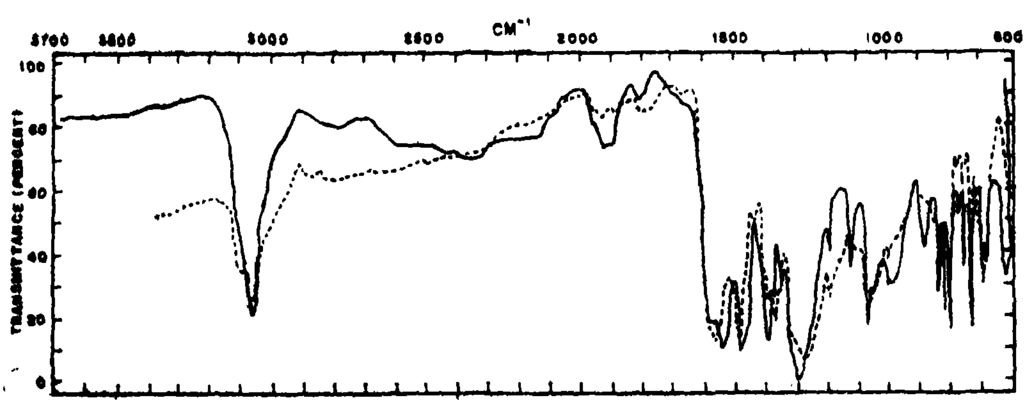


Fig. 3. —Infrared spectrum of 5-nitro-8-quinolinol-N-oxide solid (3700 cm^{-1} to 600 cm^{-1})

...The deuterated analogue.

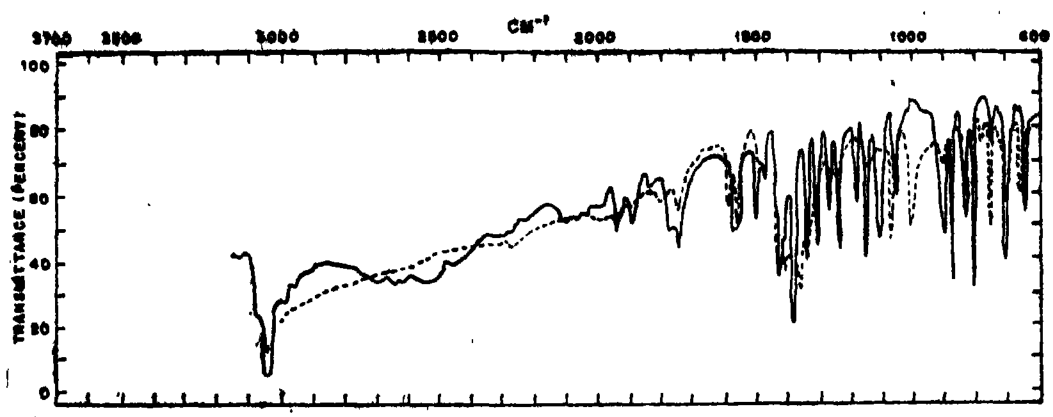


FIG. 4. —Infrared spectrum of 5, 7-dibromo-8-quinolinol-N-oxide solid (3700 cm⁻¹ to 600 cm⁻¹)
...The deuterated analogue.

2850 cm⁻¹-1800 cm⁻¹ point to the presence of strong intramolecular unsymmetrical hydrogen bond involving the hydroxyl hydrogen atom and the N-oxide oxygen atom. The hydroxyl stretching absorption ν_{OH} the inplane deformation mode coupled with C-O str. ($\delta_{OH}+\nu_{C\text{-}O}$) and the out of plane deformation mode, γ_{OH} observed in the spectra of substituted 8-quinolinol-N-oxides along with OD frequencies are given in Table 1. The ν_{NO} and δ_{NO} frequencies are observed at ca.1310-1280 cm⁻¹ and at ca.820 cm⁻¹ – 810 cm⁻¹

TABLE 1—OBSERVED I. R. ABSORPTION BANDS (cm⁻¹) IN THE REGION 2900 cm⁻¹ TO 600 cm⁻¹ IN 8-QUINOLINOL-N-OXIDES

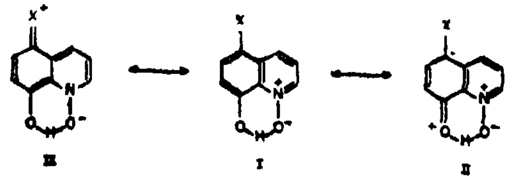
Compound	νOH	νCO+δOH	γOH
		1525 s (1295 s)	880 m (640 m)
8-HOQNO+	*2850 m (2400 m) 2540 m 2400 m (1850 w) 2240 mb 1800 w	1270 s (1000 s)	
5-NO₂, 8HOQNO	2625 m (2300 m) 2350 w,b (1800 w) 1900 w	1530 s (1260 s) 1350 s (1060 m)	800 m (650 m)
5-NO, 8HOQNO	2750 m (2300 m) 2300 m (1850 m) 1800 w	1515 m (1170 s) 1360 s (1050 s)	845 s
5-N=N C₆H₅, 8HOQNO	2600 vb (2010 w) 1850	1410 m (1260 w) 1310 s (1060 m)	870 m
5-NH₂, 8HOQNO	2600 wb 2200 w 2100 w 1900 w	1470 s (1150 m) 1275 s (1010 s)	870 m
5,7-Cl₂, 8HOQNO	—	—	1345 s (1010 s)
5,7-Br₂, 8HOQNO	2700 b,m (2060 m) 2100 w 1850 w	1470 m (1250 m) 1265 s (1000 s)	830 m (650 m)
5,7-I₂, 8HOQNO	2550 vb,w(1960 m) 1900 w	1430 s (1200 m) 1300 s (1000 s)	910 m (680 m)
5,7(NO₂)₂, 8HOQNO	940 m	—	1520 s

+8-HOQNO=8-quinolinol-N-oxide.
*The approximate centre of the broad band in the region 2850 cm⁻¹ – 1850 cm⁻¹ which shifted on deuteration. The values given in the parenthesis are the corresponding OD frequencies.
v=very, m=medium, w=weak, s=strong, b=broad.

respectively in all the spectra of the compounds and there seems to be no change in the position of these absorption frequencies.

The complex absorption pattern observed in the spectra in ν_{OH} region might arise from Fermi Resonance interaction between the hydroxyl stretching band of the strong intramolecular O-H...O hydrogen bond and other fundamental vibrational modes of the molecule and the overtone and combination bands of $(\delta_{OH}+\nu_{C-O})$. The origin of these absorptions is essentially due to anharmonicity. However, there are some other absorptions in this region which cannot be explained on the basis of Fermi Resonance only. The simplified pattern in the deutero anologues is perhaps due to the less possible number of $(\delta_{OD}+\nu_{C-O})$ and (ν_{OD}) interactions. The profiles of hydrogen stretching I. R. bands of molecules with hydrogen bonds in systems, RAH...BR′ are treated by Bratos[10] recently. It is shown that the band shaping mechanisms are the anharmonic coupling between the AH str. and different low frequency external motions and the Fermi Resonance between states involving the AH stretching and some other internal modes.

The electronic characteristics of the substituents in 5-position apparently change electron densities of both hydroxyl and the N-O oxygen resulting in variation of the strength of the H-bond. Similar effects of substituents on intramolecular hydrogen bond have been reported[11-15]. The electron withdrawing group in 5-positionwould make the intramoculelar hydrogen bond stronger by decreasing the electron density on the hydroxyl oxygen together with the enhancement of resonance from such as structure II[11]. Although one would expect the NH_2 group to weaken the hydrogen bond due to its electron donating natures, a contrary effect is observed. When electron releasing groups are at 5-position hydrogen bond also would be strengthened by the increasing in the electron density on the N-O oxygen and by the increased contribution of the structure III.



X = NO_2, NH_2, N=NC_6H_5, Cl, Br etc

The I.R. spectra of the 5,7-dinitro- and 5,7-dichloro-8-quinolinol-N-oxides do not exhibit (Figs. 1 and 2) any hydroxyl absorption in the region 2850-1600 cm^{-1}. Strong and broad absorptions at ca.1500 cm^{-1}, 1300 cm^{-1} and at ca.900 cm^{-1} are observed which show changes on deuteration. There is no band which could be assigned on the basis of usual criteria to an ν_{OH} vibration in 5, 7-dichloro compound. However, the band observed at ca.940 cm^{-1} in 5, 7-dinitro derivative in analogy with previous assignments[14] is ascribed to an ν_{OH} vibration.

Hadzi[16] had characterized two groups of short hydrogen bonds and it has been shown that in the case of the first group the barrier between the two potential minima is small enough to allow proton tunnelling resulting in the split of OH str. bands. In the second group the potential barrier is vanishingly small, the hydrogen bond approaching the symmetrical type. The ν_{OH} frequency becomes small and the characteristic property of the vibration is lost owing to strong vibrational interactions with other modes. Apparently the 5, 7-dinitro- and 5, 7-dichloro substituted-N-oxides belong to this second group. The O...O distance in 8-quinolinol-N-oxide is 2.48 Å[16] and it might be less in these 5, 7-substituted derivatives. Pimentel and McClellan[1] have distinguished three OH...O types in terms of O...O distances and observed that the range R = 2.47 – 2.54 Å is a transition region in which either type of behaviour might be found. For R below 2.47 Å the proton will display centrosymmetric distribution and above 2.54 Å the proton can be expected to be closer to one oxygen atom than the other. It is also pertinent to observe that in 5, 7-dinitro- and 5, 7-dichloro-8-quinolinol-N-oxides, the nitro or chloro groups in 7-position are increasing the non-linear O-H...O bond strength.

Acknowledgement

We wish to record our thanks to Dr. C. I. Jose for helpful discussions. One of us (K.D G.) thanks the C.S.I.R., New Delhi, for the award of a Junior Research Fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 971-973

Studies on the Dissociation Constants of Ligands at Different Ionic Strengths

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Manuscript received 6 April 1979, revised 28 February 1980, accepted 31 March 1980

The dissociation constants of salicylic acid, 5-sulphosalicylic acid, 2,2'-dipyridyl, 1,10-phenanthroline and 5-nitro-1, 10-phenanthroline have been determined in presence of KCl of varying ionic-strengths to explore the role of neutral electrolytes.

LITTLE is known regarding the effects of 'neutral electrolytes' on the dissociation constants of ligands and their complexes in view of lack of systematic attempts to explore it. The determination of the thermodynamic dissociation constants are difficult due to extremely limited or no knowledge of the activities of different constituents of the system e.g.,

$$M_xL_y \rightleftharpoons x\,M + y\,L \quad \ldots \quad (1)$$

Thermodynamic dissociation constants are generally obtained by

1) Determining the dissociation constants at infinitely dilute solutions where feasible[1].

2) Determining the dissociation constants at different ionic strengths and using various extrapolations[2-8].

3) Determining the dissociation constant at any particular ionic strength and making activity corrections using different theoretical as well as semiempirical equations which are valid at best upto 0.1 *M*[2-8].

But the exact thermodynamic dissociation constants are more or less elusive. Thus, most of the workers[4-8] prefer to use a constant "ionic medium" so that the formation constant at any particular ionic strength may be calculated. Unfortunately, the effect of different electrolytes (having the same ionic strength) on the dissociation constants are different and the comparisons of the results are also difficult unless the determinations are carried out at the same ionic strength using the same electrolytes.

Furthermore, the increased knowledge of the ion-solvent interactions have pointed to a mumber of limitations particularly when the ionic strengths are high. These are :

1) In presence of electrolytes, the solvent molecules would be highly polarised and variation of dielectric constant from 1.78 near the ions to bulk dielectric constant 78.5 would occur[9,10]. A variation of static dielectric constant of the solvent e.g., D= 71 0 in presence of 0.5 *M* LiCl to D=51.0 at 2.0 *M* LiCl at 25°[11] in presence of electrolytes is also observed.

2) The activity coefficients of uncharged electrolyte are altered to different extents in presence of different electrolytes i.e (a) CH_3COOH=1.16 in 1m NaCl and 0 97 in 1m CH_3COONa[12].

3) There is a breakdown of the tetrahedral water structure in presence of ions[13] and ions are solvated resulting in a decrease in the effective concentration of solvent molecule particularly when the electrolyte concentration is high[13-14]. Solvation of different ions are different[15].

4) Ion-association leads to the reduction of ionic-strength and association between the ions of neutral electrolyte with reacting species also lead to a number of complications.

It is thus desirable to determine the dissociation constants of ligands at different ionic strengths using different electrolytes and analyse the results in the light of observations above and explore the various factors affecting the dissociation constants of the ligands.

In order to explore the role of "neutral electrolytes" on the dissociation constants of ligands, we determined the dissociation constants of ligands of different charge types

$$BH^+ \rightleftharpoons B + H^+ \quad \ldots \quad (2)$$

B= 1, 10-phenanthroline or
5-nitro-1, 10-phenanthroline,
2, 2'-dipyridyl.

$HA \rightleftharpoons H^+ + A^-$ HA= Salicylic acid.

$HA^- \rightleftharpoons H^+ + A^=$ HA^-= 5-sulpho-salicylic acid.

in presence of "neutral electrolyte" KCl at different ionic strengths (0.03, 0.05, 0 08, 0.10, 0 20, 0.50, 1.0, 2 0 and 3.0 *M* respectively). The results are described in the present communication.

Experimental

1, 10-Phenanthroline, 2, 2′-dipyridyl, salicylic acid, 5-sulphosalicylic acid, hydrochloric acid, caustic soda, potassium chloride, acetic acid and other reagents were of G. R. (E. M.) grade. 5-Nitro-1, 10-phenanthroline (B.D.H) was used. The acids were estimated in the usual way. The solutions were prepared by dissolving the weighed quantity of the acid. In the measurement of pK values above 4.0, sodium-acetate-acetic acid buffers were used whereas for measurements of pK values below 4, HCl acid was used. KCl solutions were used to keep the ionic strength to the desired value. The solutions were made from double-distilled water.

All the ligands absorb strongly in the u.v. region and the experimental details are the same as given in earlier communications[1].

For the determination of pK values, the o.d readings of the ligands in excess acid ($N/_{10}$ HCl or more as the case may be) and in nearly neutral (in case of salicylic acid, sulphosalicylic acid) or in excess alkali ($N/_{10}$ NaOH solutions) and at intermediate pHs were taken at the analytical wave lengths. These are :

a) 310 nm and 315 nm for salicylic acid and 5-sulphosalicylic acid.

b) 300 nm and 305 nm for 2, 2′-dipyridyl.

c) 255 nm and 260 nm for 1, 10-phenanthroline.

d) 280 nm for 5-nitro 1, 10-phenanthroline.

The blank solutions were of the same composition as in the experimental solutions except the ligand.

Spectrophotometric readings were taken with a Beckman DU Spectrophotometer. pH measurements were made with a Cambridge Bench type battery operated pH-meter. All measurements were done at 25°.

Results

At any particular ionic strength, the values for the reactions (1), (2) and (3) can be represented as

$$pK = pH + \log \frac{[BH^+]}{[B]} \text{ or } pH + \log \frac{[HA]}{[A]} \quad \dots \quad (3)$$

(with appropriate charges)

The expression is ultimately written as

$$pK = pH \pm \log \frac{d - d_M}{d_i - d} \quad \dots \quad (4)$$

as the case may be, where

d_M = o.d of the molecular form

d_i = o.d of the ionic form

d = o.d at any intermediate pH at the wavelengths of measurement.

Thus, from the values of pH, d_M, d_i and d, pK values can be calculated. The results are presented in Table 1.

TABLE 1

Temp. 25° — pK-values

Ionic strength	Salicylic acid	Sulpho-salicylic acid	2,2′-Dipyridyl	1,10-Phenan-throline	5-Nitro-1,10-phenan-throline
0.03	2.97	2.78	4.61	5.11	3.29
0.05	2.96	2.74	4.63	5.15	3.29
0.08	2.94	2.63	4.63	5.13	3.30
0.10	2.93	2.48	4.75	5.12	3.36
0.20	2.91	2.46	4.75	5.23	3.55
0.50	2.76	2.29	4.82	5.28	3.59
1.00	3.14	2.10	5.32	5.30	3.72
2.00	2.94	2.11	5.45	5.39	3.43
3.00	2.62	2.13	5.61	5.49	3.70

It is to be noted in this connection that pH refers to activity of hydrogen ion concentration and $\frac{d - d_M}{d_i - d}$ refers to the ratio of the concentration of $\frac{[HA]}{[A]}$ or $\frac{[BH^+]}{[B]}$.

Discussion

In view of the absence of systematic studies of the effect of ions on the dissociation constants of ligands and complexes, it is very difficult to visualize the exact picture. The pK values at $\mu = 0.1\ M$ (with KCl, KNO_3, $NaNO_3$) range from 4.33 – 4.51 for 2, 2′-dipyridyl ; 4.8 – 5.2 for 1, 10-phenanthroline ; 2.82 – 3.00 for salicylic acid (3.70 at $\mu = 0.2\ M$ and 3.86 at 3 M $NaClO_4$) ; 2.27 – 2.49 for sulphosalicylic acid (2.67 at 3M $NaClO_4$ and 2.33 in 1.0 M KNO_3).

The thermodynamic pK_T values are :—

1, 10-phenanthroline = 4.96 – 5.05 [1,17]

2, 2′-dipyridyl = 4.47 – 4.51 [18,19]

$5\text{-}NO_2$ – 1, 10 – phenanthroline = 3.23[1,20], 3.33 (at $\mu = 0.10$)[21]

Salicylic acid = 2.97[16,22], 3.04[22]

5-Sulphosalicylic acid=2.74[16,22]
(Dissociation of the carboxyl group)

From the results given in Tables 1, it is observed that *p*K values (though not strictly concentration quotient as *p*H measures the activity of hydrogen ion) salicylic and 5-sulphosalicylic acid generally decrease as the ionic strength increases, the reverse trend is observed in case of 2, 2′-dipyridyl, 1, 10 phenanthroline and 5-nitro-1, 10-phenanthroline. It is expected as the thermodynamic values are obtained by the addition of contributions due to activity coefficients of anions or cations to *p*K values which is positive in the former case and negative in case of the latter.

In case of 'isoelectronic reactions', it is expected that 'ionic strength' should not change the *p*K values to a considerable extent. It has been actually found that the *p*K-values are more or less unchanged at low ionic strengths (upto about 0.1 *M*), but when the ionic strengths are high, a considerable change in the *p*K-values is observed. It is to be noted in this connection that *p*K values change by about 0.5 *p*K units in case of 1, 10-phenanthroline and 5-nitro-1, 10-phenanthroline but the change is about 1.0 *p*K units in case of 2, 2′-dipyridyl. It is known that both Ph and Dipy have the same type of linkages, there is difference in *p*K values obviously due to 'resonance stabilization' and fixed coplanarity in case of Ph compared to Dipy, where there is free-rotation. The greater change of *p*K-values of Dipy at higher ionic strengths might be due to the presence of highly structured solvent environment and considerable 'electrostriction'. The number of free water molecules or free-space become unavailable leading to the restriction of free rotation which ultimately increases the *p*K-values due to coplanarity.

It is to be noted that the dissociation constants as presented in the table are not true concentration quetients as the *p*Hs of the solutions measured refer to the activities of H^+ ion. Furthermore, liquid-junction potential of uncertain magnitude which increases with increase in salt concentration limits the accuracy of the determination of the stability constants.

It is very difficult to say quantitatively the exact contributions of the different factors affecting the stability constants. It is likely that the different factors may have opposing effects on the dissociation constants.

However, to have some understanding regarding the role of 'neutral electrolytes' on the dissociation consants, it is necessary to have a detailed study regarding the effect of neutral electrolyte on the activity coefficient of the different ions, the extent of possible ion-pair formation, solvation etc as enumerated earlier. Moreover, detailed study of the effect of different 'neutral electrolytes' on the dissociation constants are to be undertaken.

Acknowledgement

The authors express their sincere gratitude to U.G.C. for a scholarship and financial assistance.

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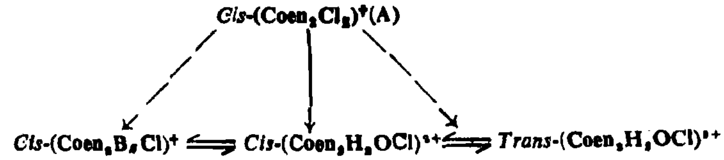
The Kinetics and Mechanism of Substitution of Chloride Ion in *Cis*-[Coen₂Cl₂]Cl by *p*-Hydroxy Benzoic Acid

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Manuscript received 23 July 1979, revised 11 February 1980, accepted 27 July 1980

The steric course of the Cl^- ion substitution in *cis* $(Coen_2Cl_2)^+$ (A) by *p*-hydroxy benzoate ion (B_z^-) was studied in 15% (v/v) ethanol at *p*H 3 and at 30° and the following mechanism has been proposed



(D) (B) (C)

Convincing evidences for the proposed mechanism was obtained by comparing the amounts of A, B, C and D at different stages of the reaction obtained by the spectrophotometric study of the reaction of B_z^- entry in A with the corresponding amounts obtained by calculation using the k-values of the different steps obtained by combination of potentiometric and spectrophotometric methods. The agreement is very good. Also the concentration of total Cl^- ion obtained from the study (potentiometric) tallies very well with the corresponding value obtained by spectrophotometric studies and calculating according to the above scheme.

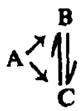
SUBSTITUTION reactions of chloride ion in *cis*-dichloro-*bis*-ethylenediamine cobalt (III) chloride by benzoic or substituted benzoic acids appear not to have been studied so far. Such a study was undertaken in the present work with a view to reveal the mechanism of these substitution reactions.

The rate of aquation of *cis*-$[Coen_2Cl_2]$ Cl (A), was studied by Mathieu[1] and Basolo *et al*[2]. The steric course of aquation of this complex was examined by Baldwin, Chan and Tobe[3], who studied the same reaction at 25° and in 0.01 (*M*) HNO_3 ; they found that the aquation of (A) proceeds with 100% retention of configuration and no *trans*-monoaquoproduct (C) is initially formed ; the initially formed *cis*-monoaquoproduct (B) is subsequently isomerised to the *trans* variety and finally a *cis-trans* equilibrium is attained (Scheme I).

$$\underset{(A)}{Cis\text{-}[Coen_2Cl_2]^+} \rightarrow \underset{(B)}{Cis\text{-}[Coen_2H_2OCl]^{2+}} \rightleftharpoons \underset{(C)}{Trans\text{-}[Coen_2H_2OCl]^{2+}}$$

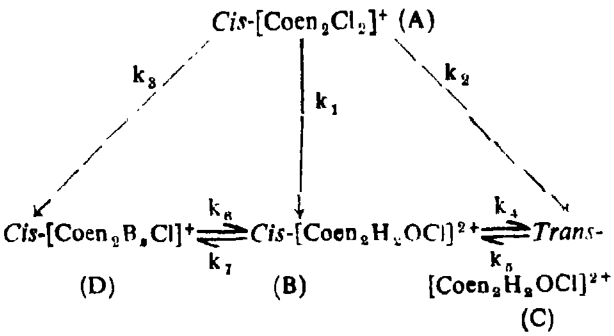
(Scheme I)

During the course of our study of the substitution reaction of Cl^- ion in (A) by parahydroxy benzoate ion (B_z^-) we have studied separately the aquation of (A) and isomerisation equilibrium of (B) and (C) in 15% (v/v) ethanol at *p*H 3 and at 30°. Our observations lead to the conclusion that during aquation, (A) is not converted 100% to (B), but both (B) and (C) are produced simultaneously and at the same time an equilibrium between (B) and (C) is established (Scheme 1A).



(Scheme IA)

When however ammonium parahydroxy benzoate is added to a solution of A in 15% (v/v) ethanol at *p*H 3, our experimental results indicate that (A) simultaneously produces (B), (C) and the *cis*mono substituted complex (D) i.e. *Cis*-$[Coen_2B_zCl]^+$ and at the same time the reversible reactions B⇄D and B⇄C come into operation (Scheme II).



(Scheme II)

Trans-$[Coen_2H_2OCl]^{2+}$ (C) however appears not to react with B_z^- directly to produce either the *trans* form of D or D itself.

In their classic text book, Basolo and pearson[4] write that the reaction mechanism for the substitution of X^- by Y^- in $[Coen_2X_2]^+$ ion always goes through the intermediate formation of the aquocomplex $[Coen_2XH_2O]^{2+}$ i.e. in the following two steps-

i) $[Coen_2X_2]^+ + H_2O—[Coen_2X.H_2O]^{2+} + X^-$

ii) $[Coen_2X.H_2O]^{2+} + Y^-—[Coen_2XY]^+ + H_2O$

the arguments being that the concentration of Y^- has no effect on the rate of Y^- entry and the aquation rate is the same as the X^- entry rate. Such a scheme would require that of the two consecutive steps i) and ii), i) is slow and ii) is very fast. However our study of the reaction ii) where $Y^- = B_z^-$ and $X = Cl^-$ shows that ii) is a slow second-order reaction the rate of which depends on $[B_z^-]$ and the second order rate constant of which is *p*H-independent and given by $k'' = 1.17 \times 10^{-3} M^{-1} Sec^{-1}$ at 30° (vide Table 1) (ii) being a slow second order reaction ; the scheme given by Basolo and Pearson in which (ii) is a very fast reaction independent of Y^- ion concentration becomes unacceptable. Moreover we have also shown that the *cis* and *trans* aquochlorocomplexes (B) and (C) are produced in large proportions simultaneously with the *p*-hydroxy benzoate substituted complex (D), when *cis*-$[Coen_2Cl_2]^+$ reacts with B_z^- in 15% (v/v) ethanol-water medium. This would have not been the case if the substitution of water by B_z^- ion in (B) and (C) were very fast, since then only insignificant amount of (B) and (C) should have existed in solution, at any stage of the reaction. Our work clearly indicates that the substitution reaction occurs in two steps, the first slow step being the formation of the intermediate pentacoordinated $[Coen_2X]^{2+}$ and the second fast step being the competetive capture of H_2O and B_z^- by this pentacoordinate intermediate. This type of mechanism in case of substitution of Cl^- from (A) by oxalate ligand had earlier been given by Ray and Siddhanta[5]. We believe that our work will serve to remove the age-old wrong idea that substitution in $[Coen_2X_2]^+$ proceeds through an intermediate step of formation of the monoaquo complex.

Experimental

(i) *Preparation of compounds* :

Cis-$[Coen_2Cl_2]Cl, H_2O$ was prepared by the method given in the literature[6]. *Cis*-$[Coen_2H_2OCl]SO_4$; $1.5H_2O$, was prepared by the method of Werner[7]. They were characterised by elemental analysis and the study of absorption spectra.

(ii) *Characterisation of products* :

When (A) reacts with B_z^- ion it gives two types of products. When (A) and ammonium *p*-hydroxy benzoate are mixed in the molar ratio 1:3 and heated on a water bath a red crystalline product is formed, the composition of which, as found by analysis, agrees with the formula $[Coen_2Bz_2]B_z$, $7H_2O$. However, when the molar ratio is 1:1, heating the solution mixture on water bath ultimately produces a sticky mass, which on prolonged digestion with dehydrated alcohol and subsequent evaporation of alcohol at room temperature gives a product of composition $[Coen_2B_zCl]Cl$. To identify whether $[Coen_2Bz_2]B_z$, $7H_2O$ and $[Coen_2B_zCl]Cl$ are of *cis* or *trans* variety, we have adopted the UV spectrophotometric method followed by Aprile, Caglioti and Illuminati[8] and found that whereas $[Coen_2Bz_2]B_z$ is of *trans* variety, $[Coen_2B_zCl]Cl$ is however of *cis*-variety. These authors have reported that at ordinary temperature the reaction between (A) and silver-benzoate in 1:3 molar proportion results in the formation of *cis*-disubstituted product which at 60-65° isomerises into the *trans* variety. Our observation that the *trans* isomer of $[Coen_2Bz_2]B_z.7H_2O$ was produced was consistent with the above, since in our case the reaction was carried out on water bath presumably at a temperature more than 60°. UV absorption spectra of all these complexes along with that of *trans* chloro aquo complex is given in Fig 1.

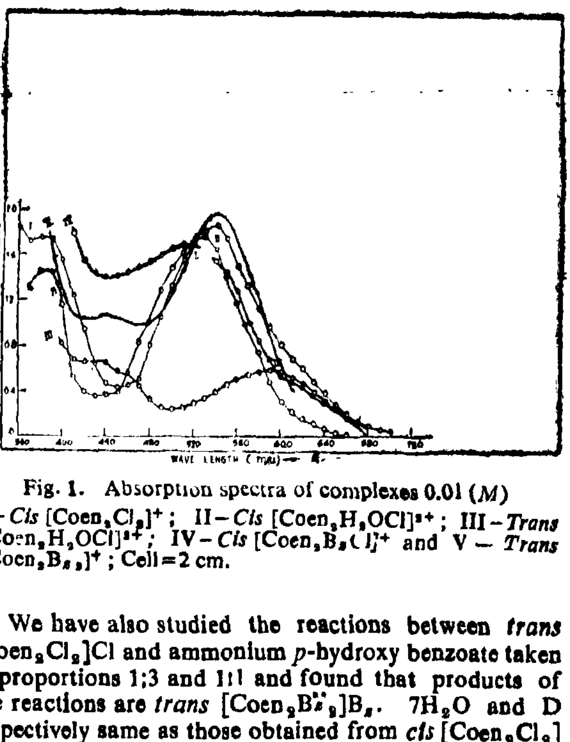


Fig. 1. Absorption spectra of complexes 0.01 (*M*) I – *Cis* $[Coen_2Cl_2]^+$; II – *Cis* $[Coen_2H_2OCl]^{2+}$; III – *Trans* $[Coen_2H_2OCl]^{2+}$; IV – *Cis* $[Coen_2B_zCl]^+$ and V – *Trans* $[Coen_2Bz_2]^+$; Cell = 2 cm.

We have also studied the reactions between *trans* $[Coen_2Cl_2]Cl$ and ammonium *p*-hydroxy benzoate taken in proportions 1;3 and 1:1 and found that products of the reactions are *trans* $[Coen_2Bz_2]B_z$. $7H_2O$ and D respectively same as those obtained from *cis* $[Coen_2Cl_2]Cl$. The products *trans*-$[Coen_2Bz_2]B_z$ and D have been obtained from reactions of the *cis*-chloro aquocomplex B with ammonium-parahydroxybenzoate taken in proportions 1:3 and 1:1 respectively. The results of the study of the Cl^- ion substitution reactions in *trans*-$[Coen_2Cl_2]Cl$ by *p*-hydroxy-benzoate ion will be communicated soon.

(iii) *Study of the Kinetics* :

The steric course of the Cl^- substitution in (A) by B_z^- ion was studied part by part and the complete study comprises of the following six parts (a) to (f)

discussed below.

[All the following studies were carried out in 15% (v/v) ethanol at a temperature 30° and $pH=3$. Lowering of pH to 3 was done to prevent the formation of aquo-hydroxo product and subsequent isomerisation[9]. The solvent was 15% ethanol, because in aqueous medium at this pH solid p-hydroxy benzoic acid begins to precipitate from 0.2 (M) solution of NH_4B_z used in the study.]

(a) *Potentiometric determination of Cl^- ion release from (A) in presence and absence of B_z^- : ($T=30°C$; $pH=3$) :*

The rate of Cl^- ion release from (A) was measured potentiometrically by noting the E. M. F. of the cell Satd.Calomel/NH_4NO_3 salt-bridge/Thermostated Reaction Mixture/AgCl, Ag, time to time and using a standard calibration curve previously drawn by plotting E.M.F. vs Cl^- ion concentration of KCl solutions of known strengths. The rate constant for the Cl^- ion release was obtained by Guggenheim plot, i.e. plot of log $(Cl_{t+\Delta t} - Cl_t)$ vs time [where $Cl_{t+\Delta t}$ and Cl_t are the concentrations of Cl^- ion at time $(t+\Delta t)$ and t respectively and Δt is a constant time interval]. It was found that the rate constant remains the same both in presence and absence of ligand B_z^-. The results are given in Table 1. This result suggests that the substitution of the first Cl^- ion in A by either H_2O or B_z^- proceeds through the same slow step namely the formation of the pentaco-ordinate intermediate $[Coen_2Cl]^{2+}$.

(b) *Isomerisation of Cis-$[Coen_2H_2OCl]^{2+}$ ion to trans form :*

$$B \underset{k_5}{\overset{k_4}{\rightleftharpoons}} C$$

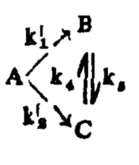
Baldwin, Chan and Tobe[3] have determined spectrophotometrically the values of k_4 and k_5 for the above reversible reaction at 25° and in 0.01(M) HNO_3. We have also determined k_4 and k_5 for the same reaction spectrophotometrically using the same method but at 30°, $pH=3$ and in 15% (v/v) ethanol-water mixture. Spectrophotometric study was made at 510 mμ where there is a maximum difference between the O.D. of the two isomers. The plot of log $(D_\infty - D_t)$ against time gave a straight line with slope (k_4+k_5) and the ratio of concentrations of C to B after attainment of equilibrium between the two gave k_4/k_5 ; the values of k_4 and k_5 were then calculated out. The results are given in Table 1.

(c) *Spectrophotometric study of the aquation of (A) and combination of this result with the results of (a).* ($T=30°C$; $pH=3$) :

The fraction of (C) produced at different times during aquation of (A) in absence of B_z^- was determined by noting the change in O.D. of the solution at 525 mμ at different times. At this wave length $\epsilon_A=\epsilon_B=89.2$ and $\epsilon_C=13.2$, hence the fractions of (C) were directly determined from the change in O.D. and the concentration C_t of C at time t could be calculated out. The concentrations B_t of B at different times t were calculated from the total chloride ion concentration (Cl_t) obtained from study (a) using the relation.

$$Cl_t = A_0 + B_t + C_t$$

Where A_0 is the initial concentration of A. The results are tabulated in Table 3. It will be seen from Table 3, last column that even from the beginning of the aquation reaction, the proportions of the *trans* product in comparison with the *cis* is not negligible ; at the end of the first ten minutes *trans* : *cis* ratio is 4:7.6. This contradicts the findings of Baldwin, Chan and Tobe[3] that the *cis* dichloro complex (A) aquates to *cis* aquochlorocomplex with 100% retention of configuration. It is more reasonable to conclude that the *cis* dichloro complex aquates by two parallel paths to both *cis* and *trans* monoaquo complexes acccording to the scheme IB.



(Scheme IB)

TABLE 1

(All studies reported in this table were made at a temperature 30°c.)

(a) *Potentiometric Study.*
$pH=3$; solvent = 15% (v/v) ethanol.
Rate constant for Cl^- ion release i.e. the rate constant for the reaction $(Coen_2Cl_2)^+ \rightarrow (Coen_2Cl)^{2+} + Cl^-$; $k=2.49\times10^{-4}$/Sec.
(Same in presence and absence of B_z^-)

(b) *Isomerisation reaction.* $B \underset{k_5}{\overset{k_4}{\rightleftharpoons}} C$
$(k_4+k_5)=1.53\times10^{-4}$/Sec. at $pH=3$ and in 15% (v/v) ethanol. $k_4/k_5=0.40$. Hence $k_4=0.44\times10^{-4}$/Sec. and $k_5=1.09\times10^{-4}$/Sec.

(c) *Spectrophotometric study of aquation of A.*
From Fig. 2 $L_{t\to0}\; B_t/C_t=1.9=k'_1/k'_2$.
But $(k'_1+k'_2)=2.49\times10^{-4}$/Sec. Hence $k'_1=1.63\times10^{-4}$/Sec. and $k'_2=0.86\times10^{-4}$/Sec.

(d) *The reaction* $B+B_z^- \xrightarrow{k_6} D+H_2O$.
At $pH=4.2$, $k_{obs}=2.223\times10^{-5}$/Sec, from which pH independent second order rate constant $k''=1.17\times10^{-2}$ litre $mole^{-1}$ sec^{-1} from where k_6 at $pH=3$ is 1.76×10^{-6}/Sec. $pK_a=4.83$ (determined by Irving Rossotti method[10] under the experimental condition.)

(e) *The reaction* $D+H_2O \xrightarrow{k_7} B+B_z^-$.
From the first order plot $k_7=5.04\times10^{-5}$/Sec.

(f) *Reaction involving entry of B_z^- in A.*
From the spectrophotometric reading at 30 minutes $D_t/B_t=k_3/k_1=0.18$.
$C_t/B_t=k_2/k_1=0.35$; but $(k_1+k_2+k_3)=2.49\times10^{-4}$/Sec. Therefore $k_1=1.63\times10^{-4}$/Sec. $k_2=0.57\times10^{-4}$/Sec. and $k_3=0.29\times10^{-4}$/Sec.

From the potentiometric study of the Cl^- ion release in absence of B_s^- [study (a)] the overall rate constant k for this reaction was found out. It is evident that this k is the sum of the two individual rate constants k'_1 and k'_2 for the parallel reactions A → B and A → C (Scheme IB) i.e. $k = k'_1 + k'_2$.

Had there been no interconversion between B and C, the ratio k'_1/k'_2 would have been equal to B_t/C_t for any time t, since B and C are the only two products of the parallel reaction. But since the interconversion of B and C influences the ratio B_t/C_t and this influence becomes greater and greater as more and more B and C accumulates with time, the true value of k'_1/k'_2 can be found out by extrapolating the values of B_t/C_t at different times to zero time i.e. using the relation—

$$\underset{t \to 0}{L_t} \frac{B_t}{C_t} = \frac{k'_1}{k'_2}$$

The ratios B_t/C_t have been plotted against t in Fig. 2, and the curve has been extrapolated to t = 0. The ratio B_t/C_t at t=0 gives $\frac{k'_1}{k'_2}$. Thus from the values of $(k'_1 + k'_2)$ and k'_1/k'_2, k'_1 and k'_2 have been calculated. The results are given in Table 1.

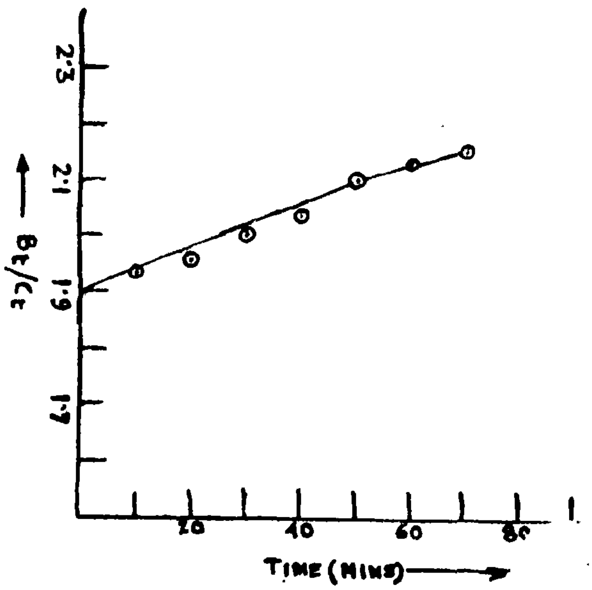


Fig. 2. Plot of B_t/C_t against time.

The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the chloride release reaction i. e. the reaction

$$Cis\text{-}[Coen_2Cl_2]^+ \xrightarrow[\text{slow}]{k} [Coen_2Cl]^{2+} + Cl^-$$

were determined by studying potentiometrically the chloride release rate constant k at different temperatures using the Eyring equation (Table 2).

TABLE 2—DETERMINATION OF ACTIVATION PARAMETERS FOR THE STEP $(Coen_2Cl_2)^+ \xrightarrow{k} (Coen_2Cl)^{2+} + Cl^-$.

	25°c.	30°c	35°c	40°C
$k \times 10^4$/Sec.	1.51	2.49	3.62	6.72

From Eyring Equation $\Delta H^{\neq} = 19.87$ K.cal/mole and $\Delta S^{\neq} = -9.85$ e.u.

(d) *Spectrophotometric study of the entry of B_s^- in B :*

$$B + B_s^- \xrightarrow{k_6} D + H_2O$$

The ligand dependance of the rate of this reaction was inferred from the fact that the rate of the forward reaction increases with increase in *p*H ; B_s^- concentration increases with increase of *p*H consequent on the shift of the equilibrium $HB_s \rightleftharpoons H^+ + B_s^-$ to the right and the rate of the reaction increases accordingly. We could not however study the reaction at *p*H 3 since the rate of the reaction was observed to be very slow. We, however studied the reaction by adjusting the *p*H to 4.2, so that the reaction rate became faster due to increase in concentration of the reacting B_s^- at this *p*H. (We used NH_4B_s as the source of the reacting B_s^- ion in the reaction.) The *p*H value remained constant at 4.2, due to the self-buffering action of NH_4B_s*.

The reaction was followed spectrophotometrically at 460 mμ (at which wave-length $\epsilon_B = \epsilon_C$) using large excess of NH_4B_s. Neglecting the influence of the backward reaction at the early stages, the pseudo-first order rate constant k_{obs} was determined by plotting $\log \frac{D_\alpha - D_0}{D_\alpha - D_t}$ against time, upto first 90 minutes. The O.D. of pure D was taken as D_α.

The following considerations show that the reactive entity at any *p*H is B_s^- and not undissociated HB_s. It will be seen from the following results that the ratio of k_{obs} at *p*H 4.2 to k_{obs} at *p*H 4.6 is equal to the ratio of $[B_s^-]$ at *p*H 4.2 to $[B_s^-]$ at *p*H 4.6 and unequal to $\frac{[HB_s] \text{ at } pH\ 4.2}{[HB_s] \text{ at } pH\ 4.6}$. The results show that the rate of B_s^- entry into the complex is proportional to $[B_s^-]$ and not to $[HB_s^-]$. This conclusion is further

*According the Basolo and Pearson[11] the equilibrium constant for the reaction $-[Coen_2ClH_2O]^{2+} + OH^- \rightleftharpoons [Coen_2ClOH]^+ + H_2O$ is 10^8 at 25°. The temperature coefficient of equilibrium constants in general being small, the equilibrium concentration of hydroxochloro species is expected to be about 1% of the concentration of the chloro-aquo species at *p*H 4.2 and 30°. As such base hydrolysis of B at *p*H 4.2 will not seriously alter the rate of the reaction $B + B_s^- \rightleftharpoons D + H_2O$ at this *p*H.

supported by the fact that at pH 3 where $[B_z^-]$ is very small and $[HB_z]$ is in large excess the reaction of $[B_z^-]$ entry into the complex is too slow to be measured. The rate of the reaction at pH 3 should have been faster than at pH 4.2 or 4.6 if $[HB_z]$ was the reactive species.

$$\frac{[B_z^-] \text{ at } pH\ 4.2}{[B_z^-] \text{ at } pH\ 4.6}=0.473 \quad \frac{[HB_z] \text{ at } pH\ 4.2}{[HB_z] \text{ at } pH\ 4.6}=1.32$$

Both calculated from K_a for $HB_z = 4.83$

$$\frac{k_{obs} \text{ at } pH\ 4.2}{k_{obs} \text{ at } pH\ 4.6}=\frac{2.223\times10^{-5}}{4.44\times10^{-5}}=0.5$$

So the above reaction is actually a second order one and the pseudo-first order rate constant k_{obs} is related to the second order rate constant k'' by the relation—

$$k_{obs}=k''(B_z^-)=k''\frac{K_a[HB_z]}{[H^+]}$$

where K_a = dissociation constant of HB_z.

By using the value of K_{obs} at pH 4.2, the second order pH independent rate constant k'' was calculated, whence the value of k_{obs} at pH 3 i.e. k_6 was calculated using the same equation. The results are given in Table 1.

(e) *Spectrophotometric study of the aquation of D* :

$$D+H_2O\xrightarrow{k_7}B+B_z^-$$

The above reaction was studied spectrophotometrically in 15% (v/v) ethanol ($pH=3$) and at 30° at 620 mμ. The first-order-rate constant k_7 was obtained by plotting log $\frac{D_\infty - D_0}{D_\infty - D_t}$ against time for the first 90 minutes, assuming that the backward reaction $B+B_z^- \rightarrow D + H_2O$ is unimportant at this stage. O.D. of pure B was taken as D_∞. In this case pH increases to 3.3 at the end. The results are given in Table 1.

(f) *Spectrophotometric study of the entry of B_z^- in A* : ($T=30°C$; $pH=3$)

When (D) was allowed to react with B_z^- (actually NH_4B_z at pH 3) at 30°, the O.D. values of the solution at 550 mμ, (at which wave length there is a substantial difference in O.D. between D and *cis* 1:3 or *trans* 1:3 product) were measured from time to time ; we found that O.D. remains constant with time, which means that under this condition practically no *cis* or *trans* 1:3 product is produced.

Next we studied the aquation of D. We found that O.D. of a solution of D changes with time at 620 mμ (Here $\epsilon_B=8$ and $\epsilon_D=23$), but a potentiometric study with Ag/AgCl electrode indicates that no Cl^- ion is released. It means that in the aquation of (D), the B_z^- ion rather than Cl^- ion in (D) is replaced by H_2O producing $[Coen_2H_2OCl]^{2+}$. Now to see whether this chloroaquo complex is (B) or (C), we studied the same aquation at 510 mμ (at this wave length $\epsilon_B \approx \epsilon_D =$ 84 and $\epsilon_C=13$) and found that O.D. remains constant with time, this means aquation of (D) produces (B) only and not (C) at all, so that it is an equilibrium between only (B) and (D) [as established in the studies (d) and (e) above]. It is thus reasonable to believe that when (B) reacts with B_z^-, it produces D only and there is 100% retention of configuration.

In order to obtain the amounts of (B), (C) and (D) and unreacted (A) at the different stages of the reaction of B_z^- entry in A, we have followed the reaction spectrophotometrically at three different wave lengths viz. 525 mμ, 450 mμ and 630 mμ simultaneously. At 525 mμ $\epsilon_A=\epsilon_B\approx\epsilon_D=89.5$ and $\epsilon_C=13$, so fall in O.D. at different stages of the reaction gave the concentrations of (C) directly at those stages.

Again at 450 mμ ($\epsilon_A\approx\epsilon_B=20.5$; $\epsilon_C=30$ and $\epsilon_D=71$), so concentration of (D) will be known from the equation—

$$\triangle d_t=\frac{C_t}{A_0}(\epsilon_C-\epsilon_A)+\frac{D_t}{A_0}(\epsilon_D-\epsilon_A)$$

$$\text{where } \triangle d_t=\frac{\text{O.D. of the reaction mixture at time t} - \text{O.D. of A at Conc. } A_0}{\text{length of the cell} \times A_0}$$

A_0 = Initial concentration of A.

C_t being known from the study at 525 mμ, D_t will be known from the above equation.

At 630 mμ ($\epsilon_A=32.5$; $\epsilon_B=6.7$; $\epsilon_C=20$; $\epsilon_D=17.5$). So B_t can be known from the measured value of $\triangle d'_t$ at 630 mμ, using the equation-

$$\triangle d'_t=\frac{B_t}{A_0}(\epsilon_B-\epsilon_A)+\frac{C_t}{A_0}(\epsilon_C-\epsilon_A)+\frac{D_t}{A_0}(\epsilon_D-\epsilon_A)$$

Thus B_t, C_t and D_t being known, A_t can be determined from the relation—

$$A_0=A_t+B_t+C_t+D_t$$

Results and Discussion

We started our study by first considering simply the aquation of A in absence of B_z^- and proved that both *B and C are produced simultaneously* by aquation and at the same time B and C produced are interconverted according to the Scheme IB.

Scheme IB was established by the following approximate method of calculating A_t, B_t and C_t at different times t, using the rate constant values obtained

from studies (a), (b) and (c) and comparing these values with experimentally determined ones of A_t, B_t and C_t (vide Table 3).

TABLE 3—COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF (B) AND (C) PRODUCED DURING AQUATION OF A. INITIAL CONCENTRATION OF A=0.01 (M)

Time (t) (mins.)	*TRANS* AQUO (C_t) M Exptl.	Calcd.	*CIS* AQUO (B_t) M Exptl.	Calcd.	Exptl. B_t/C_t
10	0.0005	0.00052	0.00096	0.00098	1.93
20	0.0010	0.00094	0.00195	0.0018	1.95
30	0.0013	0.0013	0.0026	0.0025	2.00
40	0.0016	0.0016	0.0033	0.0032	2.04
50	0.0018	0.0018	0.0039	0.0037	2.10
60	0.0020	0.0021	0.0042	0.0041	2.13
70	0.0022	0.0022	0.0048	0.0045	2.15

In our approximate calculation, we assumed that the concentration of A remains almost constant i.e. $\approx A_0$, during a brief span of time (say 10 minutes) just after the initiation of the reaction. During this period we may also neglect the equilibrium between B and C, and obtain—

$$\frac{\triangle B}{\triangle t}=k_1'A_0 \text{ and } \frac{\triangle C}{\triangle t}=k_2'A_0$$

Therefore $\triangle B = k_1'A_0\triangle t$ and $\triangle C=k_2'A_0\triangle t$

Since initial concentrations of B and C were zero therefore $\triangle B$ = concentration of B after first 10 minutes $=B_{10}$ and $\triangle C$=concentration of C after first 10 minutes$=C_{10}$. So concentration of A after first ten minutes $=(A_0-B_{10}-C_{10})=A_{10}$.

During the next ten minutes we assumed that concentration of A, B and C remain almost constant at A_{10}, B_{10} and C_{10} respectively. And here taking into consideration the interconversion of B and C also we get from Scheme IB

$$\frac{\triangle B'}{\triangle t}=k_1'A_{10}-k_4B_{10}+k_5C_{10}$$

and

$$\frac{\triangle C'}{\triangle t}=k_2'A_{10}-k_5B_{10}+k_4B_{10}$$

Thus $\triangle B'$ and $\triangle C'$ will be known and hence the concentrations of B and C after this 10 minutes i.e. 20 minutes after the begining will be—

$B_{20}=B_{10}+\triangle B'$; $C_{20}=C_{10}+\triangle C'$ and hence

$A_{20}=(A_0-B_{20}-C_{20})$.

(In this calculation, the less the time interval chosen, the greater will be the accuracy.)

In this way we calculated the values of A, B and C at different times and compared those values with the experimental values obtained during the study of aquation. The agreement is excellent (Table 3). It proves conclusively that aquation of A produces B and C simultaneously and at the same time B and C are interconverted.

From the above Scheme IB it is evident that the *cis*-complex A produces a pentacoordinate intermediate I_1 (Fig. 3) part of which immediately captures H_2O in a fast reaction to produce *cis* chloroaquo product B (k_1 path) and the rest of which in a simultaneous comparative fast reaction isomerise into the pentacoordinate intermediate I_2 (Fig. 3) and captures an H_2O molecule as if in a single step to produce *trans* aquochloro product C (k_2 path). The values of activation parameters $\triangle H^{\neq}=19.9$ K.cal/mole and $\triangle S^{\neq}=-9.9$ e.u. are in conformity with this view, since

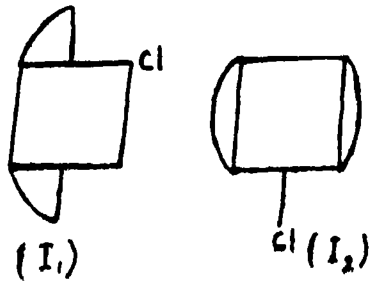
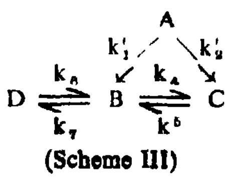


Fig. 3. Pentacoordinate intermediates I_1 and I_2.

i) $\triangle H^{\neq}$=ca. 20 K.cal/mole is of the order of M–Cl covalent bond breaking energy, and

ii) the negative value of entropy of activation may be assigned to the development of the products $(Coen_2Cl)^{2+}$ and Cl^- from $(Coen_2Cl_2)^+$ signifying a more electrostricted activated complex as compared to the reactant entity.

After establishing the Scheme IB we tried to propose a scheme for the reaction involving the entry of B_z^- in A. As Basolo and Pearson[4] have reported that with the single exception of OH^- there is no good evidence for any direct reaction of a nucleophilic reagent with a Co(III) complex in water solution and that the mechanism for the substitution proceeds in all cases through the intermediate formation of an aquo-complex, we considered the following scheme (Scheme III), in which the B_z^- substituted complex (D) is formed not directly from (A), but from the aquo-complex B [it has already been concluded from the study (f) that (D) is produced from B only and not from (C)].



(Scheme III)

We next calculated A_t, B_t, C_t and D_t at different times during the reaction course, using the already determined k values and following the above scheme. However, these calculated values differ widely (Table 4) from the spectrophotometrically determined values. The discrepencies become wider in case of D_t, where the calculated values are extremely small in comparison to the experimental values. These led us to the belief that D may be produced directly from A in addition to its being produced from B. This path seemed plausible as the first dissociative slow step of the reaction is the formation of penta-coordinate intermediate $[Coen_2Cl]^{2+}$ from A and there is every possibility of a competitive capture of both B_2^- and H_2O by this intermediate. It cannot also be doubted that this penta-coordinate intermediate is also formed from B in the first slow dissociative step which then captures competetively the ligands H_2O and B_2^- giving rise to the equilibrium $B \rightleftharpoons D$. So we have been forced to propose the Scheme II as the only plausible mechanism.

TABLE 4 – COMPARISON OF EXPERIMENTAL AND CALCULATED (ACCORDING TO SCHEME III) VALUES OF A_t, B_t, C_t AND D_t.

$A_0 = 0.01$ (*M*) concentration of $NH_4B_2 = 0.1$ (*M*), *p*H = 3.

Time (mins)	$A_t \times 10^3(M)$ Found	Calcd.	$B_t \times 10^3(M)$ Found	Calcd.	$C_t \times 10^3(M)$ Found	Calcd.	$D_t \times 10^3(M)$ Found	Calcd.
30	5.9	6.1	2.7	2.54	0.89	1.32	0.49	0.003
60	3.6	3.76	4.4	4.13	1.45	2.06	0.78	0.012
90	2.6	2.33	4.9	5.15	1.80	2.49	0.83	0.025
120	2.0	1.44	5.2	5.80	2.10	2.72	0.90	0.040
150	1.4	0.92	5.4	6.22	2.2	2.84	0.96	0.055

We then calculated theoretically the amounts of A, B, C and D at different stages of the reaction according to Scheme II using our experimental k-values. We already know the values k_4, k_5, k_6 and k_7 (as per Scheme II) from studies 'c', 'd' and 'e'; the values of k_1, k_2 and k_3 (as per Scheme II) were determined in the following way. If Scheme II is correct, then

$(k_1 + k_2 + k_3)$ = Rate constant k for the Cl^- ion release from A in presence of B_2^-.

At the early stage of the reaction (first 30 minutes) we may take $k_1 : k_2 : k_3 = [B_t] : [C_t] : [D_t]$. B_t, C_t and D_t for t = 30 mins were found out spectrophotometrically (study 'f'), whence $k_1 : k_2 : k_3$ was known; $k = k_1 + k_2 + k_3$ was experimentally found out from the potentiometric study and hence the individual values of k_1, k_2 and k_3 could be known.

Assuming that during the first 10 minutes of the reaction B, C and D are produced exclusively from A and that interconversions between B to C and between B to D can be neglected, we have

$$\frac{\Delta B}{\Delta t} = k_1 A_0 \; ; \; \frac{\Delta C}{\Delta t} = k_2 A_0 \text{ and } \frac{\Delta D}{\Delta t} = k_3 A_0 \text{ and so}$$

$$B_{10} = \Delta B = k_1 A_0 \Delta t$$

$$C_{10} = \Delta C = k_2 A_0 \Delta t$$

$$D_{10} = \Delta D = k_3 A_0 \Delta t \text{ and}$$

$$A_{10} = A_0 - (B_{10} + C_{10} + D_{10})$$

During the next 10 minutes, interconversions between B to C and between B to D also are taken in account and we write

$$\frac{\Delta B'}{\Delta t} = k_1 A_{10} - k_4 B_{10} - k_6 B_{10} + k_5 C_{10} + k_7 D_{10}$$

$$\frac{\Delta C'}{\Delta t} = k_2 A_{10} - k_5 C_{10} + k_4 B_{10}$$

$$\frac{\Delta D'}{\Delta t} = k_3 A_{10} - k_7 D_{10} + k_6 B_{10}$$

So that

$$B_{20} = B_{10} + \Delta B' \; ; \; C_{20} = C_{10} + \Delta C' \text{ and } D_{20} = D_{10} + \Delta D'$$

$$\text{and } A_{20} = A_0'' - (B_{20} + C_{20} + D_{20})$$

In this way concentration of (A), (B), (C) and (D) at different stages of the reaction was calculated. These calculated values agree very well with the corresponding spectrophotometrically determined values of A_t, B_t, C_t and D_t as obtained from study (f) and given in Table 5. Also the concentration of the total Cl^- ion at different stages of the reaction as calculated from the spectrophotometrically obtained values of (A), (B), (C) and (D) at the corresponding stages agrees excellently with the corresponding values obtained by independent potentiometric study. The results are shown in Table 5. The difference between the calculated and experimental values of A_t, B_t, C_t, D_t and Cl_t is seldom greater than 10%; the agreement should be regarded as quite good in view of the approximate nature of the experimental procedure and of the method of calculation.

TABLE 5—COMPARISON OF EXPERIMENTAL AND CALCULATED (ACCORDING TO THE SCHEME II) VALUES OF A_t, B_t, C_t AND D_t. INITIAL CONCENTRATION OF A = 0.01 (*M*) $C_{NH_4B_s}$ = 0.10 (*M*), *p*H = 3.

Time (t) (mins)	B_t(*M*)		C_t(*M*)		D_t(*M*)		A_t(*M*)		Total Cl^-_t(*M*)	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Spectro-photometric	Potentiometric
30	0.0025	0.0027	0.0009	0.0009	0.0004	0.0005	0.0062	0.0059	0.0141	0.0130
60	0.0041	0.0044	0.0015	0.0013	0.0007	0.0008	0.0038	0.0036	0.0165	0.0151
90	0.0050	0.0049	0.0018	0.0016	0.0008	0.0008	0.0024	0.0026	0.0173	0.0168
120	0.0056	0.0052	0.0021	0.0019	0.00085	0.0009	0.0015	0 0020	0.0178	0.0180
150	0.0059	0.0054	0.0022	0.0021	0.0009	0.0010	0.0010	0.0014	0.0181	0.0190

Acknowledgement

One of the authors (A.G.) is grateful to the University Grants Commission for the award of a teacher-fellowship to him.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 982-984

Effect of Medicinal Plant Gums and Other Surface Active Substances on the Particle Size Distribution of Emulsion Stabilised by Nicotine Hydrogen Tartrate

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Manuscript received 18 April 1979, revised 22 December 1979, accepted 31 March 1980

Nicotine-hydrogen-tartrate alone is not capable of giving stable emulsions with the systems, kerosene oil/water and xylene/water. Stable o/w emulsions do result with binary mixtures of nicotine-hydrogen-tartrate and gums (*dhavda* and *salai*), other adjuvants such as cetyl-trimethyl ammonium bromide (CTMAB), sodium lauryl sulphate(SLS), saponin, gelatin. Lecithin can not be recommended as good emulsifying agent. The nature of internal phase plays an important role as it is evident from the globule size distribution, practically as well as graphically determined initial specific interfacial areas and stability coefficient values.

PLANT-DERIVED poisons are generally characterised by their greater safety for use on plant foliage than most inorganic compounds. The structure or form of the compounds is usually rather easily broken down into harmless bodies. The alkaloid nicotine is basic in reaction levorotatory, volatile and much more toxic in this form than when combined with acids (dextrorotatory) to form non-volatile or fixed compounds[1].

Richardson and Shepard[2] found that nicotine as the free base was from 5 to 7 times as toxic as nicotine sulphate or hydrochloride when tested against mosquito larvae, but Starr and Richardson[3] comparing 1-nicotine d-tartrate against 1-nicotine, found the former to be slightly (possibly not significantly) more toxic than the latter.

The volatile nicotine sprays and dusts are used principally against soft bodied insects, including aphids, thrips, psyllids, tingids, poultry lice, a very few of the beetles and young lepidopterous larvae and sawflies.

Fixed or stable nicotine compounds are of permanent or residual type that is effective over a period of many days. They may be injected by feeding on coated leaves or act as a repellent to prevent feeding and induce migration. Non-volatile compounds have been used principally against codling moth (*Carpoeapsa pomonella*)[4,5,6], grapebery moth (*Polychrosis oitecona*), pistol case-bearer (*Coleophora malivorella*)[7] and citrus thrips[8].

A survey of the literature reveals that no work has been done on the emulsifying capability of nicotine-hydrogentartrate. In continuation with the previous work on insecticides and medicinal plant gums of India in the present work it is intended to study the effect of addition of a few Indian medicinal plant gums and other surface active substances on the particle size distribution and stability of emulsions stabilised with nicotine-hydrogen tartrate.

Experimental

The emulsions were prepared using nicotine hydrogen tartrate to contain 40% (kerosene oil or xylene) as the internal phase. Emulsions were also prepared by adding the minimum quantity of purified gum or other adjuvant to the fixed quantity of nicotine-hydrogen-tartrate in 60 c.c. of water. The suspensions were made by slightly warming at 60 - 80° over a water bath. Then the emulsions were made in the usual manner as described by Mukerjee and Shukla[9].

The size frequency analyses were made immediately and at different intervals of time by the method of King and Mukerjee[10]. The change of specific surface was plotted against time as abscissa for several emulsions to illustrate the agreement between the data on the change of specific surface with time and exponential hypothesis. The lines were determined by fitting the data to the equation :

$$-\frac{d\sigma}{dt} = K'\sigma = \frac{\sigma}{K}$$

(where σ = specific surface, K' = instability coefficient and K = stability coefficient) by the method of *least squares*[11,12]. The curves representing the degradation of the emulsions are all linear ; hence a measure of the slope provides a quantitative comparison of stability. Accordingly, the slope of each curve has been measured and divided by the graphically determined initial interface (σ_0) to furnish the rate of decrease per unit area

of interface. This is termed as the instability factor and might be defined as the decrease of each cm^2 of fresh emulsion per day. The reciprocal of this would be a direct measure of emulsion stability.

Results and Discussion

Emulsions were prepared using kerosene oil and xylene, stabilised by nicotine-hydrogen-tartrate as emulsifying agent. Different percentages of Indian medicinal plant gums and other adjuvants were also tried as emulsion stabilisers. The results are too numerous to quote in full. Only the summarised results have been given in Table 1. A few representative curves between particle diameter and percentage of particles have been depicted in Fig. 1.

TABLE 1—DATA FOR 40% KEROSENE OIL AND XYLENE EMULSIONS

Emulsion no.	Agents	KEROSENE OIL: Initial specific area $\times 10^{-3}$ — Experimental	KEROSENE OIL: Initial specific area $\times 10^{-3}$ — Graphically determined	KEROSENE OIL: Stability coefficient $K \times 10^3$	Emulsion no.	XYLENE: Initial specific area $\times 10^3$ — Experimental	XYLENE: Initial specific area $\times 10^3$ — Graphically determined	XYLENE: Stability coefficient $K \times 10^3$
1.	0.5% Nicotine hydrogen tartrate + 0.5% Dhavda Gum	4.90 cm^2/gm	4.36 cm^2/gm	11.97	13.	4.34 cm^2/gm	3.89 cm^2/gm	18.30
2.	0.5% Nicotine hydrogen tartrate + 0.1% Dhavda Gum	—	—	broken	14.	3.95	—	broken
3.	0.5% Nicotine hydrogen tartrate + 0.5% Salai Gum	4.70	4.41	13.57	15.	5.28	4.67	9.16
4.	0.5% Nicotine hydrogen tartrate + 0.05% Saponin	9.57	7.67	9.47	16.	6.17	5.24	10.74
5.	0.5% Nicotine hydrogen tartrate + 0.02% Saponin	7.87	5.62	7.19	17.	5.55	4.95	10.61
6.	0.5% Nicotine hydrogen tartrate + 0.1% Gelatin	4.90	4.57	7.03	18.	4.57	4.16	5.32
7.	0.5% Nicotine hydrogen tartrate + 0.05% Gelatin	4.51	4.26	6.08	19.	4.18	3.83	5.21
8.	0.5% Nicotine hydrogen tartrate + 0.1% Sodium Lauryl Sulphate	9.86	7.67	10.17	20.	9.55	7.32	15.69
9.	0.5% Nicotine hydrogen tartrate + 0.05% Sodium Lauryl Sulphate	9.58	7.41	8.48	21.	6.13	—	broken
10.	0.5% Nicotine hydrogen tartrate + 0.1% Cetyl-trimethyl ammonium bromide	7.04	5.30	25.96	22.	5.83	5.55	17.60
11.	0.5% Nicotine hydrogen tartrate + 0.05% Cetyl-trimethyl ammonium bromide	3.97	3.75	21.26	23.	5.82	5.24	12.34
12.	0.5% Nicotine hydrogen tartrate + 0.6% Lecithin	3.73	3.23	0.15	24.	—	—	broken



Fig. 1. Distribution of Particle Sizes in Emulsions

O – First day – Emulsion No. 12
● – One week – Emulsion No. 12
× – First day – Emulsion No. 1
■ – First day – Emulsion No. 13

Nicotine-hydrogen-tartrate itself was not found to be a suitable emulsifying agent for kerosene/water or xylene/water systems. But when appropriate quantities of Indian gums and other adjuvants as listed in Table 1, were used along with nicotine-hydrogen-tartrate stable emulsions were produced.

Size frequency analyses of kerosene emulsions stabilised by different agents reveal that saponin, sodium lauryl sulphate and cetyl trimethyl ammonium bromide in combination with nicotine-hydrogen-tartrate produced very fine emulsions. Finest emulsions were produced with saponin as emulsifying agent as can be seen from the experimental initial specific area value 9.57 and also graphically determined initial specific area (Table 1 emulsion no. 4).

Dhavda and Salai gums, along with gelatin produced emulsions having initial specific areas 4.90, 4.70, 4.90, Lecithin produced very fine emulsion. In this case globule size distribution on the first day of preparation and after one week's storage time has been ploted in Fig. 1. It is evident from the size distribution curve that in this case the emulsion is very fine. It remains so even after storage of one week although there is change in the percentage of fine particles after storage. The other two cases (Emulsion no. 1 and 13) represent some what coarse emulsions as the no. of smaller particles has been decreased still further.

The stability coefficient values can be arranged in the following order:

CTMAB > Salai gum > Dhavda gum > SLS > Saponin > Gelatin > Lecithin.

Xylene emulsion, stabilised with sodium lauryl sulphate (SLS) had very fine globule distribution as is evident from the initial specific area value of 9.55. The order of fineness of the particle was found to be:

S L S > Saponin > CTMAB > Salai gum > Gelatin > Dhavda gum.

The graphically determined initial specific area also changed in the same order. With the change of internal phase the stability coefficient values were changed in the following order:

Dhavda gum > CTMAB > SLS > Saponin > Salai gum > Gelatin > Lecithin.

In general it can be concluded that CTMAB, Dhavda gum and saponin produced the most stable emulsions with all the systems. Salai gum also produced stable emulsions with kerosene oil as internal phase. Lecithin can not be recommended as a good emulsifying agent. Of course the internal phase plays an important role.

Acknowledgement

One of the authors A. K. V. acknowledges with thanks the SCST (U P) for financial assistance. The authors are grateful to the Head of Chemistry Department, Lucknow University for providing necessary facilities.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 985-990

Thermodynamic Parameters and Stability Constants of Cu(II), Ni(II), Co(II), Zn(II), Pd(II), Rh(III) and Pt(IV) Complexes with Diaminoacetyl Urea

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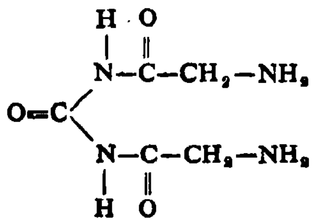
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Manuscript received 21 August 1978, revised 9 November 1979, accepted 13 May 1980

The stability constants of the complexes of copper(II), nickel(II), cobalt(II), zinc(II), palladium(II), rhodium(III) and platinum(IV) with diaminoacetyl urea are reported. The order of decreasing stability of divalent metal is $Pd^{+2} > Cu^{+2} > Zn^{+2} > Co^{+2} > Ni^{+2}$. The stepwise changes in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) values for complexation are evaluated in different ionic strengths (0.15*M*, 0.125*M*, 0.1*M* and 0.075*M*) and at different temperatures $(25 \pm 0.02)°$ and $(30 \pm 0.02)°$. The standard $\triangle G°$, $\triangle H°$ and $\triangle S°$ are also calculated at zero ionic strength. The nature of the co-valent bonding in the complexes have been discussed in detail.

ALTHOUGH stability constants values for interaction of metal ions with complexing ligands are generally reported in literature, there are few corresponding thermodynamic constants $\triangle G$, $\triangle H$ and $\triangle S$ values available. Such data are useful in evaluating the relative importance of thermodynamic constants in determining the magnitude of stability constant and understanding the factors which contributes to the complex formation.

Diaminoacetyl urea (hereafter abbreviated as DAAU) forms complexes with many metal ions[1,2,3]. The reagent has been used for spectrophotometric study of metal ions. In view of the great potentialities of the NH_2 group as analytical reagent, it is desirable to study its physico-chemical aspects.



Structure I : DAAU

In the present communication, the stability constants and thermodynamic parameters of the complexes of copper(II), nickel(II), cobalt(II), zinc(II), palladium(II), rhodium(III) and platinum(IV) with DAAU in aqueous solution have been studied in different ionic strengths (0.15*M*, 0.125*M*, 0.10*M* and 0.075*M*) and at temperatures. $(25 \pm 0.02)°$ and $(30 \pm 0.02)°$.

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Experimental

DAAU was prepared by the procedure described in an earlier paper[1]. The stock solution of metal ions were prepared by dissolving copper sulphate, nickel sulphate, cobalt sulphate, zinc sulphate, palladium chloride, rhodium chloride and chloroplatinic acid. Sodium hydroxide (0.1*M*) solution was made by dissolving AR(BDH) NaOH pellets in carbondioxide free distilled water and was standardised with standard solution of oxalic acid.

The titrations were carried out in an inert atmosphere by bubbling the nitrogen gas through the solution. The *p*H measurements were carried out with the solution maintaining four different ionic strengths (0.15*M*, 0.125*M*, 0.1*M* and 0.075*M*) which were achieved by adding requisite quantity of 0.1 *M* sodium perchlorate and perchloric acid.

Solution mixture containing (a) acid (0.01*M* perchloric acid +0.1*M* sodium perchlorate), (b) ligand (mixture 'a' and 25 ml of 0.1*M* DAAU) and (c) complex (mixture 'b' and 5 ml of 0.01*M* metal solution) were taken and total volume was kept 50 ml. The mixtures (a), (b) and (c) were separately titrated against standard 0.1*M* sodium hydroxide.

*p*H measurements were done by Phillips *p*H meter using glass calomel electrode assembly at constant temperatures 25 $(\pm 0.02)°$ and 30 $(\pm 0.02)°$.

Method and Calculations: The stability constants were determined, using the Bjerrum-Calvin technique[4,5] as adopted by Irving[6] and Rossotti[7].

Thermodynamic Constant :

Thermodynamic constant values of overall changes in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$), accompanying complexation, have been calculated with the help of standard equations.

$$\triangle G = -RT \ln \beta$$

and

$$\triangle S = \frac{\triangle H - \triangle G}{T}$$

The values of $\triangle H$ were calculated at each temperature interval by the relationship

$$\triangle H = \frac{2.303\, R\, T_1\, T_2 \log K_2/K_1}{(T_2 - T_1)}$$

Results

The values of $\bar{n}_H$ (the number of proton attached to the ligand), $\bar{n}$ (the number of ligand molecule attached to central metal ions) and P_L (negative logarithm of the anion of the ligand) were calculated by using Irving and Rossotti expressions[7] :

The DAAU showed a maxima of one for $\bar{n}_H$, the dissociation constant (pK) of the ligand was calculated from pH value corresponding to $\bar{n}_H = 0.5$ at different ionic strengths and different temperatures. The formation curves were drawn by plotting $\bar{n}$ and P_L values. The stepwise formation constants log K_1 and log K_2 were calculated from the P_L values corresponding $\bar{n}$ = 0.5 and 1.5 respectively at different temperatures (25° and 30°) and at various ionic strengths (μ=0.15 M, 0.125 M, 0.10 M and 0.075 M).

The thermodynamic dissociation constants and formation constants were obtained by determination at various ionic strengths, followed by extrapolation to zero ionic strength[21]. The sum of log K_1 and log K_2 at μ=0 gives the value of log β at μ=0. The values of log β (overall concentration formation constants) were likewise extrapolated to zero ionic strength. The thermodynamic parameters that were calculated from stability constants are listed in Table 3.

Discussion

The dissociation constants of the ligand DAAU and stability constants of the complexes obtained at different temperatures (25±0.02)° and (30±0.02)° and various ionic strengths are given in Tables 1 and 2. From the

TABLE 1—PROTONATION CONSTANTS OF LIGAND DAAU

Ionic strength (μ)	pK_1 at 25°C	pK_1 at 30°C
0.15 M	9.65	9.50
0.125 M	9.70	9.60
0.1 M	9.80	9.70
0.075 M	9.85	9.75
0.0 M	10.05	9.95

TABLE 2—STABILITY CONSTANTS OF METAL CHELATES OF DAAU

Metal ions	Stability Constants	Temperature 25°C μ=0.15M	0.12M	0.10M	0.075M	μ=0	Temperature 30°C μ=0.15M	0.12M	0.10M	0.075M	μ=0
Cu(II)	log K_1	10.06	10.12	10.25	10.32	10.70	9.82	9.85	9.95	10.20	10.40
	log K_2	6.31	6.38	6.50	6.72	7.00	6.01	6.11	6.15	6 20	6.45
	log β	16.37	16.50	16.75	17.04	17.70	15.83	15.96	16.10	16.40	16.85
Ni(II)	log K_1	9.72	9.80	10.05	10.20	10.45	9.52	9.60	9.65	9.82	9.90
	log K_2	5.86	5.90	5 95	6.10	6.15	5.75	5.80	5.80	5.85	5.85
	log β	15.58	15.70	16.00	16.30	16.60	15.27	15.40	15.45	15.67	15.75
Co(II)	log K_1	9.80	9.82	9 90	10.10	10.30	9.65	9.80	9.95	10.00	10.05
	log K_2	5.95	6.00	6.15	6.20	6.40	6.00	6.10	6.20	6.25	6.45
	log β	15.75	15.82	16.35	16.30	16.70	15.65	15.90	16.15	16.25	16.50
Zn(II)	log K_1	9.95	10.05	10.15	10.20	10.50	9.85	9.90	10.00	10.10	10.30
	log K_2	6.00	6.10	6.20	6.25	6 45	5.85	5.95	6.15	6.20	6.40
	log β	15.95	16.15	16.35	16.45	16.95	15.70	15.85	16.15	16.30	16.70
Pd(II)	log K_1	10.55	10.60	10.75	10.80	11.15	10.00	10.10	10.75	10.70	10.85
	log K_2	6.40	6.45	6.50	6.65	6.70	6.35	6.40	6.50	6.52	6.60
	log β	16 95	17.05	17.25	17.45	17.85	16.35	16.50	16.75	17.22	17.45
Rh(III)	log K_1	9.55	9.60	9.75	9.95	10.20	9.35	9.30	9.65	9.65	10.10
	log K_2	4.85	5.00	5.15	5.30	5.75	4.75	4.90	5.00	5.10	5.45
	log β	14.40	14.60	14.90	15.25	15.95	14.10	14.40	14.65	14.95	15.55
Pt(IV)	log K_1	10.80	10.85	10.90	11.05	11.10	10.65	10.75	10.75	10.95	11.10
	log K_2	6.52	6.55	6.70	6.85	6.95	6.30	6.42	6.45	6.60	6.85
	log β	17.82	17.40	17.60	17.90	18.05	16.95	17.17	17.20	17.50	17.95

structure of DAAU it reveals that it has two-NH_2 groups and two NH groups between two $-C{=}O$ groups. The liberation of hydrogen from NH_2 group is more possible than $-NH$ group. At higher pH value, the alkali reaction liberates both hydrogen ions simultaneously. Thus only one protonation constants is expected upto certain range of pH value. Similar observations were also reported in case of biuret[8]. The stability order of the divalent metal complexes in all ionic strengths studied here is $Pd^{+2} > Cu^{+2} > Zn^{+2} > Co^{+2} > Ni^{+2}$, except for cobalt ion, the order is the same as in Irving Williams series[9]. Such type of abnormal behaviour by cobalt were also reported earlier[10,11]. Johnston and Freiser[12] reported similar observations in their investigations on metal complexes of 8-OH-2-methyl quinoline. The higher stability of the cobalt complex was attributed to higher oxidation state of cobalt in the complex. The oxidation of Co(II) to Co(III) has taken place in the present investigation during complex formation. Such behaviour of cobalt with DAAU is already communicated[8]. The variation of the stability of the complexes of divalent metal ions may be represented by plotting log β against atomic number and second ionization potential of the metal (Fig. 1.) Such correlation, were made by

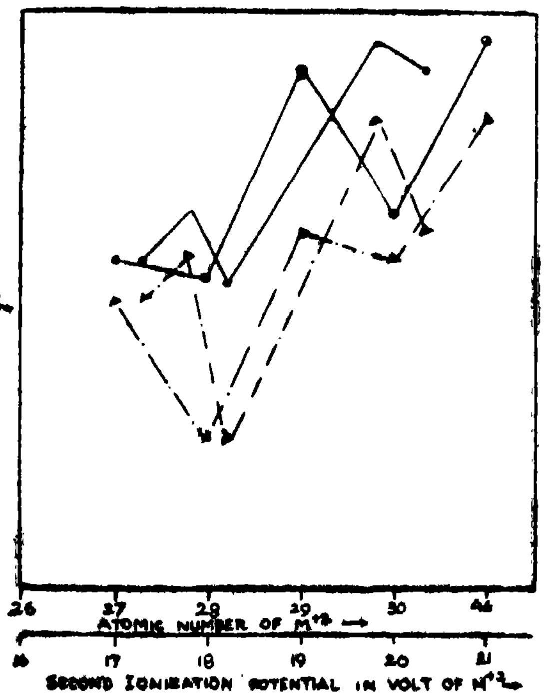


Fig. 1. The plot of log β (at $\mu = 0$) vs atomic number of divalent metal ion and second ionization potential in volt of M^{+2}.

⊙ – ⊙ log β vs atomic number at 25°C
▲ – ▲ log β vs atomic number at 30°C
● – ● log β vs 2nd ionization potential at 25°C
▲ – ▲ log β vs 2nd ionization potential at 30°C

Calvin and Melchior[13] for the formation of metal chelates of 5-salicylaldehyde sulphonate. The low value of stability constant of Zn^{+2} than Cu^{+2} may be explained on the basis of the following factors : (a) d-orbital, which is not taking part in homopolar bond formation, (b) ionic radii and (c) due to higher charge density of electron around the metal ion. The plot of χ_m (electronegativity of metal) against log β (Fig. 2) shows

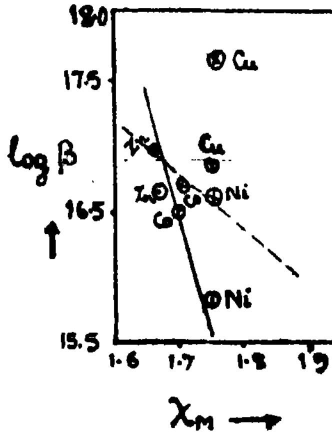


Fig. 2. The plot of electronegativity (χ_m) vs overall stability constant (log β).

⊙ - ⊙ at 25°C
⊗ – ⊗ at 30°C

roughly a linear relationship. It may be inferred that the greater stability of metal complex with increasing χ_m value and metal ligand bond would be more covalent. Similar observations have been reported by Vanuitert[14] and Seibin[15]. The plot of log β against reciprocal of ionic radii of transition metals $\left(\frac{1}{r_{cryst}}\right)$ (Fig. 3), show that the ligand forms most unstable

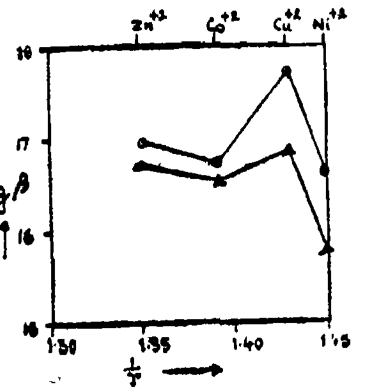


Fig. 3. The plot of reciprocal of ionic radii vs log β (at $\mu = 0$)

⊙ - ⊙ at 25°C
▲ – ▲ at 30°C

complex with nickel(II) metal and stabler complex with copper II) than other divalent transition metals. The presence of π bond of M-L may be explained on the basis of high positive value of the log K_1/K_2. Similar results have been reported in literature[4] and can be assumed to be due to a combination of factors such as static, steric hindrance.

The standard ΔG°, ΔH° and ΔS° values which are obtained from extrapolated value of the stability constants to zero ionic strength are listed in Table 3.

TABLE 3—THERMODYNAMIC CONSTANTS OF METAL INTERACTION OF DAAU

Metal Ion		ΔG° (Free energy) K cal/mole at $\mu=0$ 25°C	30°C	ΔH° (enthalpy) at $\mu=0$ K cal/mole	ΔS° (entropy) at $\mu=0$ K cal/degree mole
Cu^{+2}	log K_1	−14.59	−14.41	−24.79	−0.15470
	log K_2	9.54	−9 94	−45.45	
	log β	−24.13	−23.36	−70.24	
Ni^{+2}	log K_1	−14.38	−13.72	−45.45	−0.15976
	log K_2	−8.38	−8 11	−24 79	
	log β	−22.63	−21.83	−70.24	
Co^{+2}	log K_1	−14.04	−13.93	−20 65	+0.02095
	log K_2	−8.72	−8.94	+4.13	
	log β	−22.77	−22.87	−16.52	
Zn^{+2}	log K_1	−14.31	−14.28	−16 52	+0.00825
	log K_2	−8.79	−8.87	−4.13	
	log β	−23.11	−23.15	−20.65	
Pd^{+2}	log K_1	−15.20	−15 04	−24.79	−0.02923
	log K_2	−9 13	−9.15	−8.26	
	log β	−24.33	−24.19	−35.05	
Rh^{+2}	log K_1	−13.90	−14.00	−8.26	−0.03792
	log K_2	−7.84	−7.55	−24 79	
	log β	−21.75	−21.56	−33.05	
Pt^{+4}	log K_1	−15 13	−15.39	−0.0	+0.05485
	log K_2	−9.47	−9.49	−8.26	
	log β	−24.60	−24.88	−8.26	

It is of interest to compare the stability constants value with standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The linear relationships are obtained (Figs. 4,5,6). The enthalpy for complex species ΔH° (log K_1) is more negative than the value of ΔH° (log

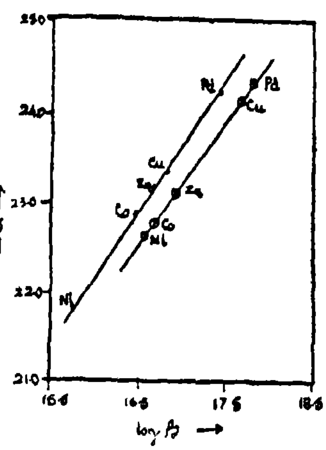


Fig. 4. The plot of ΔG° vs log β (at $\mu=0$)
● ● at 25°C
⊙ – ⊙ at 30°C

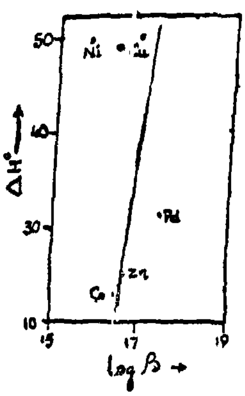


Fig. 5. The plot of ΔH° vs log β (at $\mu=0$)

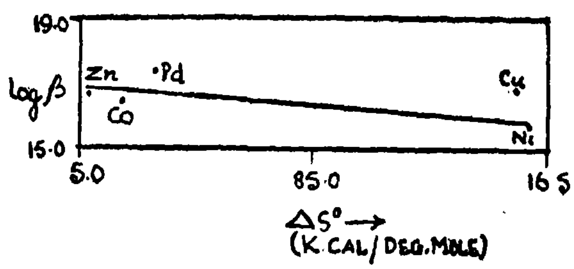


Fig. 6. The plot of ΔS° vs log β

K_2). The enthalpy corresponding to the formation of complexes are exothermic. There is a regular change in the value of ΔH° for complexes in series of divalent metal ion, except in case of cobalt complex in which ΔH° (log K_2) value is positive. The abnormal behaviour of cobalt is already reported above. A positive value of ΔH° (log K_2) of cobalt may be due to high heat of hydration. To study the bonding nature of the complexes it is necessary to observe the relation between ionic radii of metal against thermodynamic parameters. The plot of the thermodynamic parameters ΔG°, ΔH° and ΔS° against $\frac{1}{r}$ (ionic radii) of divalent transition metal, (Figs. 7,8,9), show good linear relationship. Thus entropy of the complex species for divalent metal ion studied are proportional to the reciprocal of their ionic radii. Martell[16] has suggested a dependence linear relationship between ΔS° and $\frac{1}{r}$ for divalent metals. Similar observations were reported by Stavely[17] for EDTA complexes. This indicates the predominant role of electrostatic forces involved in the ion-association processes, a fact which is in harmony with Bjerrum original ion pair concept. Martell and Khan[18] have studied similar linearity by plot of ΔS° against $(r_a+r_c)^{-1}$ where r_a and r_c are the anionic and cationic radii respectively. From Table 3 the relatively small ΔH° values compared with large value of ΔS° indicates entropy as the principal driving force for formation of metal complexes, in aqueous solution. The positive value of the entropy in case of cobalt and zinc, reflecting the release of coordinated water molecules from interacting ions because of the partial or complete change of the neutralization. The number of coordinated negative

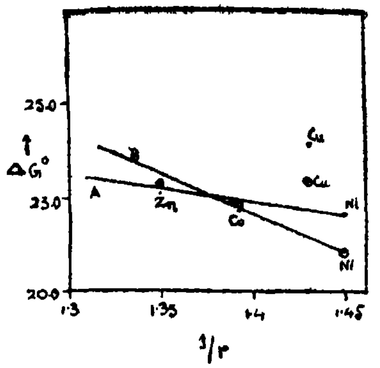


Fig. 7. The plot of $\Delta G°$ vs 1/r
A ●—● At temp. 25°C
B ⊙—⊙ At temp. 30°C

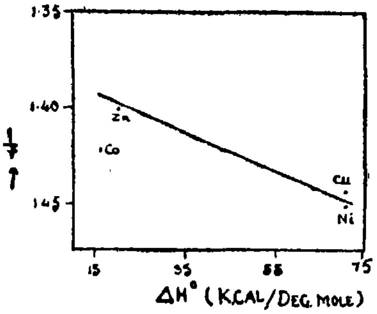


Fig. 8. The plot of $\Delta H°$ vs 1/r

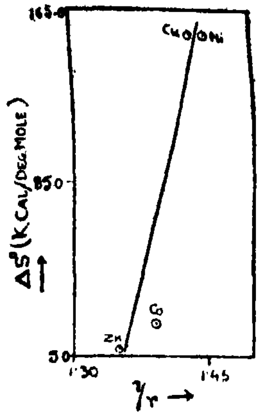


Fig. 9. The plot of $\Delta S°$ vs 1/r

donor group (Ze) and electronegativity of the metal ion (χ_m) have been correlated with the effective radii of metal ion, in the present study. The correlation between effective radius of metal ion and electronegativity as given by equation below, is indicated in Table 4 and illustrated graphically in Fig. 10.

$$r_e = r_p + 0.48 + 0.14Ze \ \chi_m.$$

TABLE 4—CORRELATION OF THE EFFECTIVE RADIUS OF THE METAL ION WITH ELECTRONEGATIVITY

Divalent metal ion	r_a	x_M	r_e	$r_e - r_p$
Co	0.72	1.70	2.152	1.45
Ni	0.69	1.75	2.15	1.46
Cu	0.65	1.75	2.11	1.46
Zn	0.74	1.66	2.15	1.41

r_p = Pauling ionic radii, r_e = effective ionic raddii (angstrom unit),
x_M = Electronegativity of metal ion on Allred-Rochow scale.

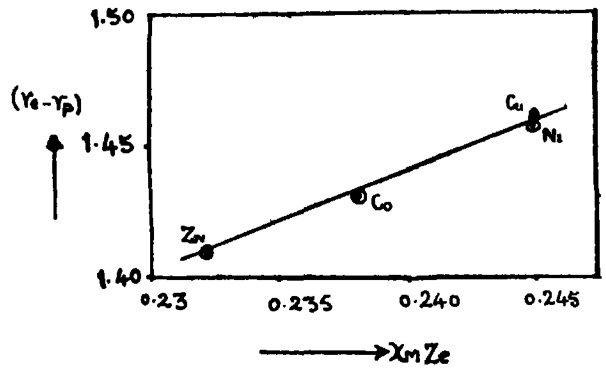


Fig. 10. Correlation of the effective radius of the metal ion with electronegativity.

where r_e is the effective radius of the metal ions, χ_m their electronegativity on the Allred-Rochow[19] scale, and r_p is Pauling crystal radius in angstrom. Such relationship indicates better understanding of covalent nature of the complexes. Such correlations have also been reported in case of adenosine diphosphoric and adnosine monophosphoric acid metal complexes[20].

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 991-994

Solute-Solvent Interactions in Solutions of Potassium Acetate in Water and Aqueous Methyl Acetate

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Manuscript received 15 January 1979, revised 24 January 1980, accepted 31 March 1980

Gross solute-solvent interaction in solutions of potassium acetate in water and in aqueous methyl acetate (20% by weight) has been deduced from the values of apparent molar volume determined by precise density measurement, relative viscosity and the B-coefficient of the Jones-Dole equation and from conductance studies at different concentrations and at 25°, 30°, 40° and 50°. It is found that the salt behaves as structure maker in water and in aqueous methyl acetate.

SOLUTE-solvent interaction studies have been a subject of active interest among physical chemists[1-6] and mostly the inferences regarding these interactions are drawn from conductance[7], molar volume data[8] and viscosity data[9,10] together. Literature is full of such studies in pure solvents. Studies in mixed solvents are of considerable interest because peculiar results are obtained[11] in most of the solvent systems. The present study is carried out in connection with the work on physico-chemical studies of systems involving acetates and the main object of the paper has been to arrive at the nature of solute-solvent interaction from the molar volume, viscous flow and conductance properties of potassium acetate in water and aqueous methyl acetate (when one of the constituents of the solute and solvent has some common features).

Experimental

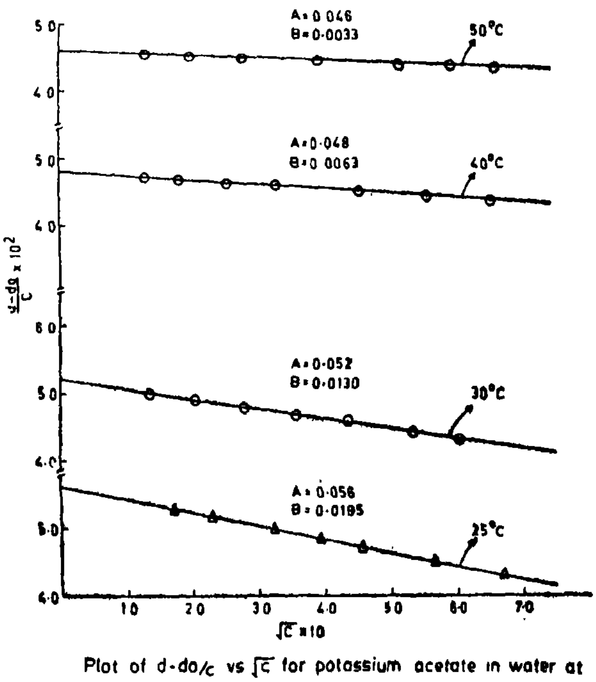
Potassium acetate was used after crystallisation from anhydrous acetic acid and pumped dry under vacuum for 30 hours at 100°. Methyl acetate was purified by treating with potassium carbonate and later distilled after keeping for an overnight over P_2O_5. The conductivity, density and viscosity of methyl acetate at 30° used were 3.8×10^{-6} $ohm^{-1}cm^{-1}$, 0.92065 $g.ml^{-1}$ and 0.00351 poise respectively and these values agree with literature values[12,13]. The water conductivity of order 10^{-6} $ohm^{-1}cm^{-1}$ was used for making 20% (by weight) aqueous methyl acetate. The density[14], viscosity measurements[9] and conductance[15] measurements were carried out by the method described earlier. All measurements except of viscosity were made in the water bath placed in an air thermostat with temperature fluctuations always below 0.02°. In case of viscosity, measurements were carried out in air thermostat having temperature fluctuations of the order ±0.05°. The viscosity of the water used for calculation were 0.8937 cp, 0.8007 cp, 0.656 cp and 0.5494 cp at 25°, 30°, 40° and 50° respectively. The densities were taken as given in the literature[12].

Results and Discussion

The density of the various solutions, d, can be represented by the Root's equation[16] :

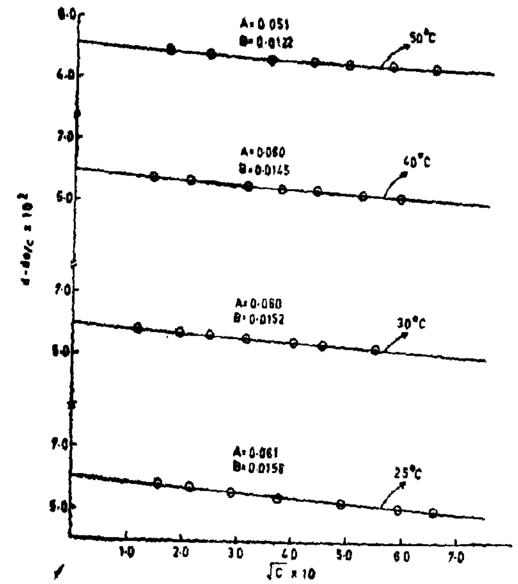
$$d = d_0 + AC - BC^{3/2} \tag{1}$$

where d_0 is the density of the solvent, C is the concentration, and A and B are the constants of the Root's equation. On plotting $d-d_0/C$ versus $\sqrt{C}$ a straight line should be obtained and we get straight line in each case as shown in Figs. 1 and 2. Values of A and B



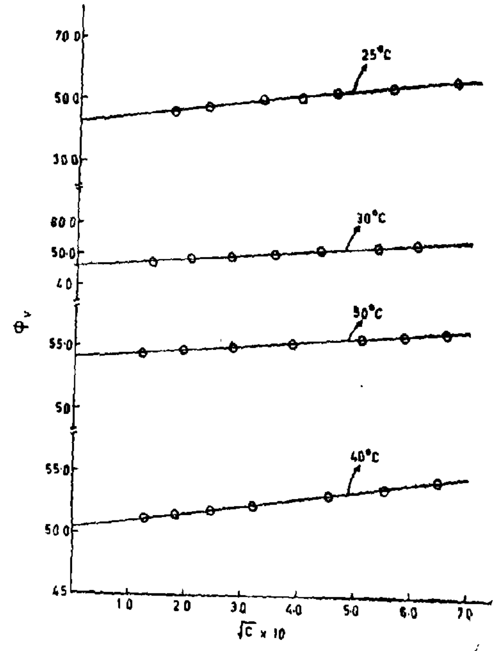
Plot of $d-d_0/C$ vs $\sqrt{C}$ for potassium acetate in water at different temperatures

Fig. 1



Plot of d-d₀/c vs $\sqrt{c}$ for potassium acetate in aqueous methyl acetate (20%) at different temperatures

Fig. 2



Plot of ϕ_v vs $\sqrt{c}$ for potassium acetate in water at different temperatures

Fig. 3

evaluated from the intercept and slope of the plots are given with the ligands of the graph 1 and 2.

The apparent molar volume, ϕ_v°, is calculated from the density data by the equation[17] :

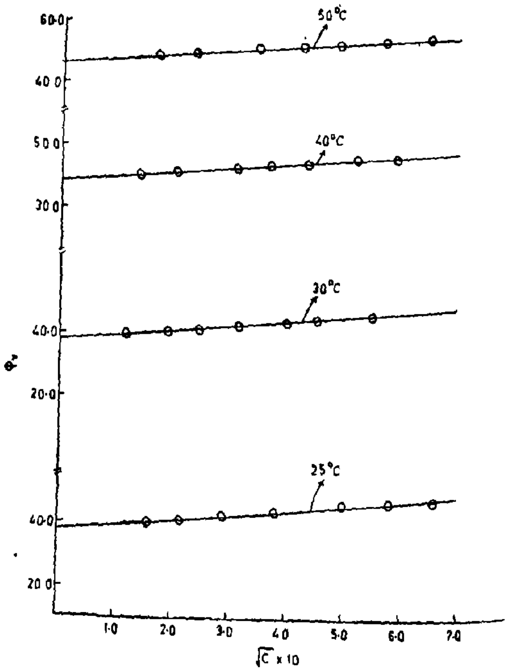
$$\phi_v = \frac{1000(d_0 - d)}{m\, d\, d_0} + \frac{M_2}{d} \qquad (2)$$

where ϕ_v represents the molar volume of the electrolyte, d the density of the solution, d_0 the density of the solvent, m is the molality of the solutions and M_2 the molecular weight of the electrolyte.

The apparent molar volume has been found to vary with concentration according to Masson's equation[18] and the data can be represented by the relation :

$$\phi_v = \phi_v^\circ + S_v \sqrt{C} \qquad (3)$$

where ϕ_v° is the limiting apparent molar volume, and S_v is the experimental slope. Here ϕ_v° is a measure of solute-solvent interaction and S_v is a measure of ion-ion interaction. The limiting apparent molar volume, ϕ_v°, for different systems calculated from the linear graph of ϕ_v versus $\sqrt{C}$ as shown in Figs. 3 and 4 are given in Table 1.



Plot of ϕ_v vs $\sqrt{c}$ for potassium acetate in aqueous methyl acetate (20%) at different temperatures

Fig. 4

The greater magnitude of ϕ_v° in case of water suggests that the solute-solvent interaction is greater in case of water. Further, Table 1 shows that it increases with increase of temperature in water and aqueous methyl acetate. The increase in the ϕ_v° of potassium acetate in water and in aqueous methyl acetate with increasing temperature may be attributed to the increase

TABLE 1—VALUE OF ϕ_v^0 FOR DIFFERENT SYSTEMS.

System	Temperature (°C)	ϕ_v^0 (ml.mol^{-1}
Potassium acetate in water	25	42.80
	30	46.10
	40	51.00
	50	54.01
Potassium acetate in aqueous methyl acetate (20%)	25	38.00
	30	38.50
	40	38.80
	50	46.50

in the solute-solvent interactions. The temperature coefficient $(\partial\phi_v^0/\partial t)$ increases with increase of temperature[19] in both the solvents. Using Hepler's reasoning of long-range intereactions, we find that potassium acetate behaves as a structure maker because $(\partial^2\phi_v^0/\partial t^2)$ is positive, and the accommodation of the solute in the void space left in the packing of the large associated solvent molecules and the greater solvation of inorganic ions with methyl acetate is not unexpected.

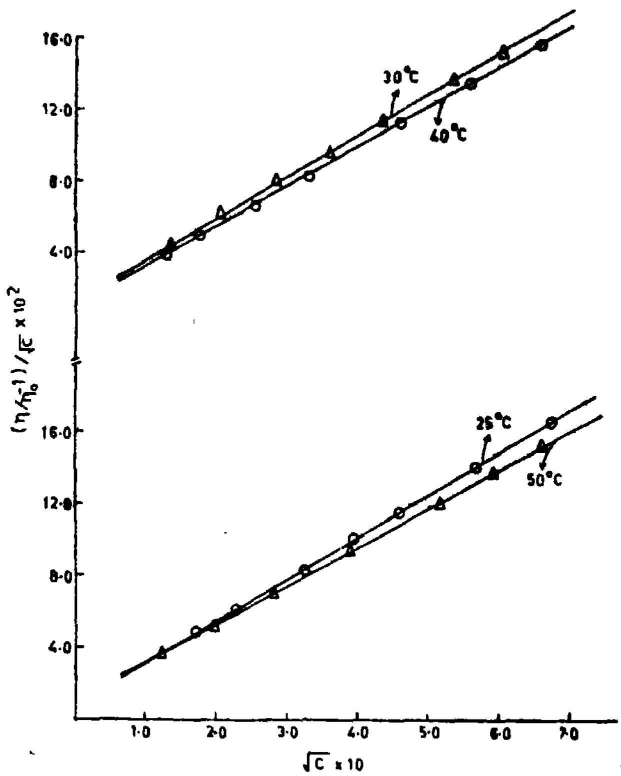
The data on viscosity was analysed with the help of the Jones-Dole[20] equation :

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \qquad (4)$$

where η is the viscosity of the solution, η_0 is the viscosity of the solvent, C is the molar concentration and A and B are constants characteristic of the solute electrolyte. A coefficient represents the contribution from interionic electrostatic force[21]. The B coefficient is said to be a measure of the effective hydrodynamic volume of the solvated ions[22] and to denote the order or disorder introduced by the ions into the solvent structure. The values of A and B of equation (4) are determined from the intercept and slope of the straight line plots of $(\eta/\eta_0 - 1)/\sqrt{C}$ versus $\sqrt{C}$ as shown in Figs. 5 and 6. Values of A and B parameters at different temperatures are given in Table 2.

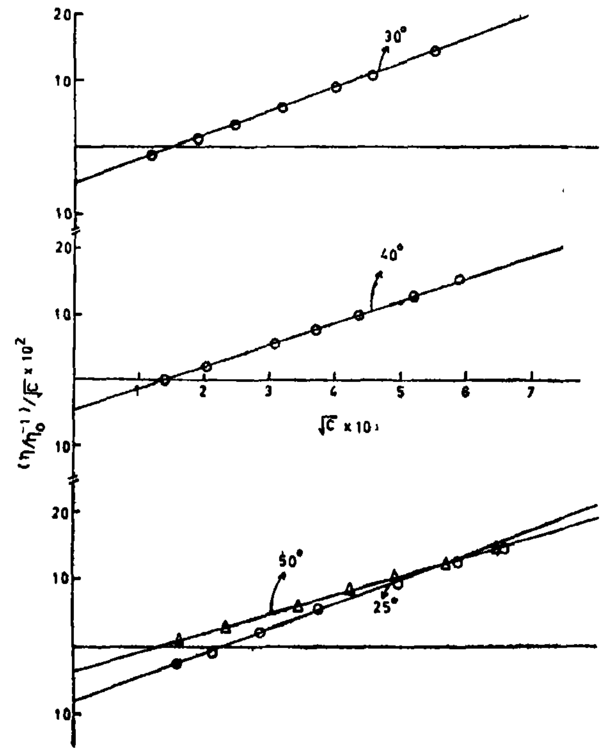
TABLE 2—JONES-DOLE PARAMETERS AT DIFFERENT TEMPERATURES FOR DIFFERENT SYSTEMS.

System	Temperature (°C)	A	B
Potassium acetate in water	25	0.008	0.237
	30	0.010	0.234
	40	0.010	0.226
	50	0.010	0.214
Potassium acetate in 20% methyl acetate	25	−0.009	0.370
	30	−0.006	0.357
	40	−0.005	0.333
	50	−0.004	0.280



Test of Jones-Dole equation for potassium acetate in water at different temperatures

Fig. 5



Test of Jones-Dole equation for potassium acetate in aqueous methyl acetate (20%) at different temperatures

Fig. 6

In the Jones–Dole equation, A is a calculable parameter and is similar for all 1:1 electrolytes. The A-parameter was found to be slightly higher than the observed value of 0.0066 for lithium acetate in water by Laurence and Wolfenden[23] and Cox and Wolfenden[24] obtained +0.238 as the value of the B-coefficient which is in good agreement with the value obtained in the present investigation. The negative temperature coefficient of B-parameter dB/dT suggests that the salt behaves like a structure maker[25] in case of water.

In case of solutions of aqueous methyl acetate negative values of A have been obtained and such negative values have been obtained in most of the cases involving mixed solvents[26,27]. The negative temperature coefficient of B, dB/dT suggests that the salt behaves as a structure maker in the aqueous methyl acetate. The large B-coefficient in aqueous methyl acetate (20%) shows that a large ion behaves as more obstacle (than in water) in a way similar to that of a colloidal particle.

The limiting equivalent conductance, Λ_0, at different temperatures is evaluated from Onsager's plots[28], and with the help of Owen's method[29]. This is based on the conductance equation :

$$\Lambda = \Lambda_0 - SC^{\frac{1}{2}} + AC\log C + BC \qquad (5)$$

where S is the limiting Onsager slope, C is the concentration, A and B are constants.

The limiting equivalent conductance, Λ_0, along with the Walden product, $\Lambda_0\eta_0$, is given in the Table 3.

TABLE 3—LIMITING EQUIVALENT CONDUCTANCE, Λ_0, WALDEN PRODUCT, $\Lambda_0\eta_0$, FOR POTASSIUM ACETATE

Temperature (°C)	Λ_0 (Onsager) ($ohm^{-1}cm^2$)	Λ_0 (Owen) ($ohm^{-1}cm^2$)	$\Lambda_0\eta_0$
	Water		
25	116.50	114.75	1.0[illegible]2
30	140.50	137.50	1.097
40	172.50	169.30	1.111
50	215.00	211.00	1.159
	20% Aqueous Methyl Acetate		
25	104.00	102.40	1.207
30	138.00	134.50	1.307
40	164.00	161.50	1.340
50	202.00	196.80	1.354

The structural effect on the conductance of ions in solutions can be derived by a comparison of the Walden product($\Lambda_0\eta_0$) at different temperatures[25]. The positive temperature coefficient of the Walden product in both the systems suggests that salt behaves like a structure maker. These conclusions are in agreement with those derived from viscosity measurements.

Acknowledgement

One of the authors (P.C.V.) is thankful to the Council of Scientific and Industrial Research for the award of a Senior Research Fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 995-998

Thermochromic Behavior of Buffered Indicator Solutions
I. Determination of the Heat of Proton Ionization of Phenolphthalein

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Manuscript received 25 March 1980, accepted 27 July 1980

The apparent heat of proton ionization, $\triangle H'$, for phenolphthalein in aqueous solutions containing 6 per cent ethanol by weight was determined by two methods, (a) the conventional spectrophotometric method in which apparent dissociation constants are obtained as a function of temperature and (b) the novel thermochromic method. The reasonably good agreement between the results of the two methods establishes the latter as a powerful and unique tool for obtaining $\triangle H'$ values of weak acids.

IN an earlier publication[1], one of us (F. H. Jumean) reported on a system whose absorbance was a highly sensitive function of temperature. The system consisted of an aqueous 0 1 M glycine solution to which was added a small amount of ethanolic phenolphthalein solution and sufficient 0.1 M NaOH to bring the pH up to the second acidic pK of the aminoacid. It was then employed, however, as a 'chemical thermometer' for the purpose of measuring temperatures during the course of investigating the thermal behavior of myoglobin solutions, and no attempt was made to examine its thermodynamic properties. In a later presentation[2], however, some of the thermodynamic properties of buffered indicator solutions were described. In this paper, we report on the first of a series of current experimental investigations of the thermodynamic properties of such solutions.

In a system consisting of a buffer HB and an indicator HIn the principal equilibria are

$$HB = B + H^+ \quad \text{... (1)}$$

$$HIn = In^- + H^+ \quad \text{... (2)}$$

For the case in which the change in the heat capacity, $\triangle C_p$, for both buffer and indicator is assumed to be zero, application of the familiar Van't Hoff expression

$$\log K = -\frac{\triangle H}{2.303\ RT} + \text{constant} \quad \text{... (3)}$$

readily yields the following expression

$$\log \frac{a_{In^-} \cdot a_{HB}}{a_{HIn} \cdot a_{B^-}} = \frac{-(\triangle H_B - \triangle H_I)}{2.303\ RT} + \text{constant} \quad \text{...(4)}$$

in which the symbol a denotes activity and $\triangle H_B$ and $\triangle H_I$ are the heats of proton ionization of buffer and indicator, respectively.

If the mixed system is investigated at a pH equal, or close to, the pK of the buffer then the ratio a_{HB}/a_{B^-} should remain essentially constant upon varying the temperature despite the accompanying pH changes, provided that the buffer concentration is sufficiently high to ensure good buffering capacity. Furthermore, since indicator concentrations are typically very small (in this study *ca.* 3×10^{-5} M), activities of indicator species may be replaced by concentrations and equation (4) becomes

$$\log \frac{[In^-]}{[HIn]} = \frac{b}{T} + at \quad \text{... (5)}$$

where $b = -(\triangle H_I - \triangle H_B)/2.303$ R and the term a is constant. The left handside of equation (5) is accessible from spectrophotometric measurements and a plot of this quantity against 1/T should have a slope equivalent to the term b. Thus, if either one of the $\triangle H$ values is known from independent mesurements, the other may be obtained by employing the thermochromic method. In this paper we report on our attempt to investigate the usefulness and applicability of this method with respect to the common indicator phenolphthalein. Three buffers whose pK values lie within the transformation range of this indicator (pH 8-10) were selected *viz*. glycine, isoleucine, and phenol.

Experimental

All chemicals were of reagent grade and were used without further purification. Distilled deionized water

was used for the preparation of all solutions. *p*H measurements were conducted on an Orion research microprocessor Ionalyzer model 501 equipped with calomel and glass electrodes. The instrument was calibrated using two standard boric acid-NaOH buffer solutions. The calibration was repeated every time the temperature was altered, making use of the reported value[3] of -0.0082 for the temperature coefficient (d*p*H/dT) of the standard buffer. The reliability of the measurement was better than 0.01 *p*H unit. Spectrophotometric measurements were conducted on a Pye-Unicam SP 8000 spectrophotometer equipped with a thermostatted cell compartment. The temperature inside the cell was continuously monitored to within 0.2° by means of a thermocouple.

Due to the extremely low solubility of phenolphthalein in water, all measurements were carried out on aqueous solutions containing 6 percent ethanol by weight. This condition necessitated the determination of the heats of ionization of three buffers in this medium, since changes in the dielectric constant of the medium have been known to affect values of apparent dissociation constants as well as heats of proton ionization of weak acids[4].

Results and Discussion

Apparent macroscopic dissociation constants, *p*K′ values, for glycine, isoleucine, and phenol were determined in aqueous solutions containing 6 per cent ethanol by weight at an ionic strength of 0.100*M*. The standard procedure of titrating 0.1*M* solutions of the weak acid in a thermostatted cell against standard 0.1*M* sodium hydroxide solution was employed. The experimental *p*K′ values are plotted in Fig. 1 against the reciprocal of the absolute temperature. The plots for glycine (a) and isoleucine (b) are fairly linear, yielding apparent heats of ionization, $\triangle H'$, values, of 10.58 and 11.50 Kcal/mole, respectively. The literature values in purely aqueous solutions of the same ionic strength are 10.75 Kcal/mole for glycine[5] and 11.15 Kcal/mole for isoleucine (estimated from data in ref. 6). Furthermore, the good linearity of plots a and b of Fig. 1 is in accord with the reported small $\triangle C_p$ value[5] of -12 cal/deg. mole for glycine and the likewise small value of -15 cal/deg. mole for isoleucine (also estimated from data in ref. 6). The close agreement between our $\triangle H'$ values for the two aminoacids in the present medium and the literature values for purely aqueous solutions may be readily attributed to the well-known existence of these acids in the predominant zwitterionic form. The proton ionization of a zwitterionic aminoacid is not accompanied by any net change in the total charge, and hence the medium effect upon the energy of this process ought to be very small.

Fig. 1(c) is a similar plot for the temperature dependence of *p*K′ for phenol. The somewhat concave appearance of this plot indicates that $\triangle C'_p$ for phenol, unlike that for the two aminoacids, is significant. Analysis of p the plotted results yields the following expression for the temperature dependence of $\triangle H'$ for phenol :

$$\triangle H' = 5130 - 60\ (T\text{-}25) \qquad \ldots (6)$$

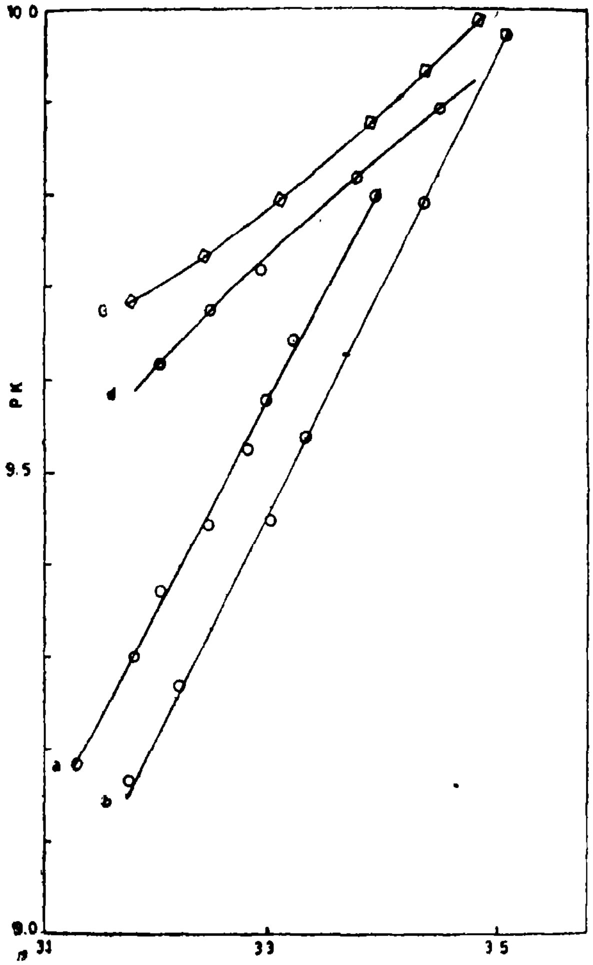


Fig. 1. Plot of *p*K′ *vs.* 1/T for a) glycine, b) isoleucine, c) phenol and d) phenolphthalein.

in which $\triangle H'_{25}{}^\circ$ = 5130 cal/mole and $\triangle C'_p$ = -60 cal/deg. mole. Two observations seem pertinent at this point. Firstly, our $\triangle H'_{25}{}^\circ$ value for phenol is significantly lower than the literature value of 6.1 Kcal/mole[7] in aqueous solution at the same ionic strength. This observation must be solely attributed to the change in medium (see reference 4, for example, for a discussion of medium effects). Secondly, our $\triangle C'_p$, value is more negative than the value of -43 cal/deg. mole in aqueous medium[6], an obeservation which is consonant with the general trend of decreasing $\triangle C_p$ with decreasing dielectric constant of the medium[4]. A detailed discussion of the medium effect is, however, outside the scope of this work, since the primary aim is to obtain reliable values of $\triangle H'$ from a conventional method for comparison with other values obtained from the thermochromic method.

pK' values for for phenolphthalein were obtained over a 30° temperature range by employing the conventional spectrophotometric method in which the optical densities of solutions equimolar in the indicator concentration were measured as a function of pH in the vicinity of the indicator's pK. The following equation was applied :

$$pK' = pH - \log \frac{D - D_a}{D_b - D} \quad \dots \quad (7)$$

where D is the optical density of the solution at the pH of interest and D_a and D_b are the optical densities of the same solution in very acidic and very basic media, respectively. All measurements were carried out on solutions buffered with boric acid-NaOH buffer containing equimolar concentrations (3.50×10^{-5} M) of the indicator and 6 per cent ethanol by weight. Changes in optical density were monitored at 550 nm, the wavelength maximum of the basic form (In^-) band, at which D_a was equal to zero. It may be noted that log terms of equations (5) and (7) are identical. Fig. 1(d) shows the temperature dependence of pK' for phenolphthalein. The slight convexity of the plot indicates that $\triangle C_p'$ for the indicator is small and positive, but the limited accuracy of the data does not justify an expression analogous to equation (6). The slope of this plot yields a value of 3.92 ± 0.1 Kcal/mole for $\triangle H'$ of the indicator.

In Table 1 the various $\triangle H'$ values in the present medium are listed alongside the literature values in aqueous solution.

TABLE 1

$\triangle H'$, Kcal/mole

Compound	This work[a]	Literature[b]	Reference
Glycine	10.58	10.75	5
Isoleucine	11.50	11.15	5[c]
Phenol	5.13	6.1	6
Phenolphthalein	3.92	—	—

a. aq. sol'n containing 6 per cent ethanol by weight, $I = 0.00M$
$\triangle H'$ values accurate to within ± 0.05 Kcal/mole

b. aq. sol'n, $I = 0.100$ M

c. estimated value

Thermochromic Results : Fig. 2 shows the temperature dependence of the optical density at 550 nm for solutions containing equimolar ($2.36 \times 10^{-5} M$) concentrations of phenolphthalein and each of the three weak acids under the same conditions of the previous experiments. The pH values for these solutions were somewhat different because of differences in the pK' values between the three weak acids. Inspection of Fig. 2 reveals that the magnitude of the change in optical density for glycine (a) and isoleucine (b) is considerable, whereas that for phenol (c) is slight and accompanied with the appearance of a minimum. This observation

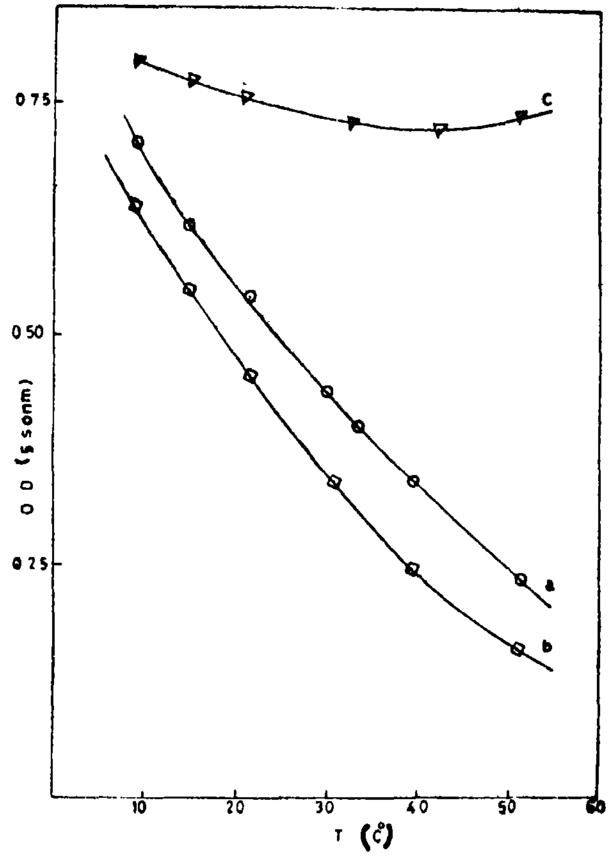


Fig. 2. Typical plots of the dependence of optical density on temperature for indicator solutions containing a) glycine, b) isoleucine and c) phenol.

is in line with the finding (Table 1) that $\triangle H'_B - \triangle H'_I$ values for indicator solutions of the two aminoacids are considerably greater than the corresponding value for phenol. The appearance of a minimum in curve (c) at *ca.* 43° is interesting. At this temperature, $\triangle H'_{43°}$ for phenol is only 4.05 Kcal/mole (from equation 6) and considering that $\triangle H'$ for phenolphthalein was found to have an average value of 3.92 Kcal/mole in the temperature range investigated, this confirms the finding, *vide supra*, that $\triangle C'_p$ for phenolphthalein is small and positive, since at the temperature of minimum optical density the value of the term b is clearly zero (see equation 5).

Fig. 3 is a plot of equation (5) for indicator solutions containing glycine (a), isoleucine (b) and phenol (c). Plots (a) and (b) show good linearity and yield respectively, values of 6.86 and 7.67 Kcal/mole for the quantity $\triangle H'_B - \triangle H'_I$. Since $\triangle H'_B$ values have already been independently determined for the two aminoacids in the same medium (Table 1), two separate values for $\triangle H'_I$ may now be calculated : 3.72 Kcal/mole from the glycine solutions and 3.87 Kcal/mole

from the isoleucine solution. These values are in reasonably good agreement with the value of 3.92 Kcal/mole obtained from the conventional spectrophotometric method.

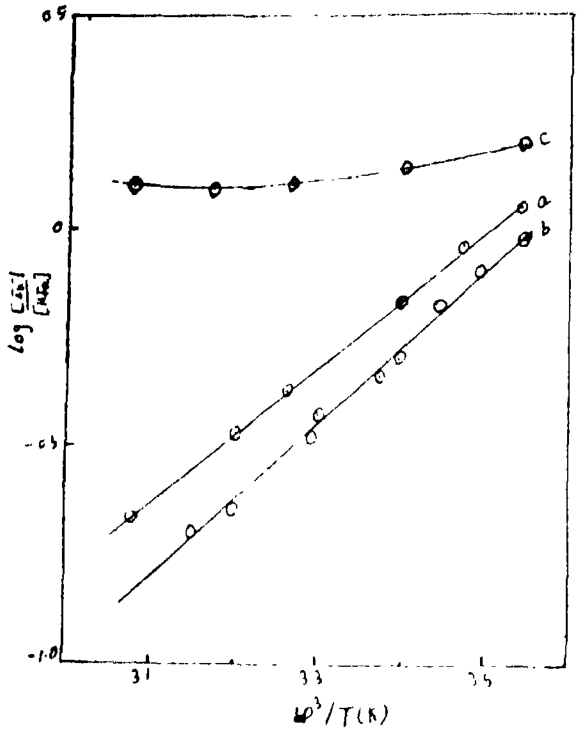


Fig. 3. Plot of equation (5) for indicator solutions with a) glycine, b) isoleucine and c) phenol.

The plot of equation (5) for the phenol-phenolphthalein system, however, is somewhat concave. This behavior indicates that the b value decreases with increasing temperature and ought to be expected from the thermal behavior of this system (Fig. 2, c). At 25°, the slope of this plot yields the value of 1.29 Kcal/mole for the quantity $\triangle H'_{H} - \triangle H'_{I}$. Since $\triangle H'_{H}$ for phenol has already been independently determined with a value of 5.13 Kcal/mole (Table 1), the calculated value for $\triangle H'_{I}$ would be 3.84 Kcal/mole, again in good agreement with experimental results already presented.

Table 2 summarizes the various $\triangle H'_{I}$ values obtained in this work.

In conclusion, it may be stated that the application of the thermochromic method to the determination of the heats of proton ionization of weak acids has been

TABLE 2

System	$\triangle H'_{In} \pm 0.1$, Kcal/mole	Method
Glycine-In	3.72	Thermochromic
Isoleucine-In	3.87	Thermochromic
Phenol-In	3.84	Thermochromic
Boric acid-NaOH-In	3.92	Conventional spectrophotometric

In=Phenolphthalein, I=0.100 *M*. All solutions contain 6 per cent ethanol by weight.

shown to yield good and consistent results. The advantages of this method lie in its speed, since no prior *p*K determination is required, as well as in its reasonable accuracy. The existence of a wide variety of indicators with transition intervals spanning the entire *p*H range ensure the wide applicability of this method. In a following report we shall deal with systems of large $\triangle C_p$ values and modify equation (5) to make it applicable to such systems.

Acknowledgement

The authors wish to thank the University of Jordan for financial support and Dr. E. S. Awad, for reviewing the manuscript.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 999-1001

Ionic Equilibria in Aqueous Solutions of Zinc Bromide and the Related Heat Data

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Manuscript received 25 April 1980, accepted 26 July 1980

The dissociation constant of $ZnBr^+ \rightleftharpoons Zn^{++} + Br^-$ has been determined potentiometrically and has been found to be 0.2559, 0.0573, 0.0973 and 0.0339 at 5°, 15°, 25° and 35° respectively. The heat of ionisation ΔH of $ZnBr^+ = Zn^{++} + Br^-$ has been found to be +1331±100 cals/mole.

FERRELL, Ridgion and Riley[1] studied potentiometrically the behaviour of zinc bromide in aqueous solution and suggested the possibility of complex ion formation. Parton and Mitchell[2] considered zinc bromide to be completely dissociated up to 0.1 *M*. Egan and Partington[3] concluded that zinc bromide behaves as a strong electrolyte up to the concentration range 0.36 molarity. Stokes, Stokes and Robinson's[4] studies showed that zinc bromide does not dissociate completely even up to 0.1*M*. Stokes and Stokes[5] has reported that it is not permissible to regard zinc bromide as fully dissociated even at 0.1*M*. On account of the different conclusions of the authors, it was decided to study the dissociation of zinc bromide.

Up to 0.1μ, it was assumed that the first stage of dissociation of zinc bromide is complete.

Ist stage

$$ZnBr_2 \rightleftharpoons ZnBr^+ + Br^-$$

2nd stage

$$ZnBr^+ \rightleftharpoons Zn^{++} + Br^-$$

Experimental

Analar grade zinc bromide was not available. Hence zinc carbonate was first precipitated by adding hot solution of A.R. sodium carbonate in slight excess to hot zinc chloride (A.R.) solution. The precipitate was washed about 40 times in almost boiling water to remove the chloride completely, though the presence of chloride ion was found to be absent much earlier. Zinc carbonate was dissolved in G.R. hydrobromic acid and a stock solution of zinc bromide in hydrobromic acid was prepared. The zinc and the bromide contents of the solution were respectively estimated gravimetrically by the oxine[6] and volumetrically by Volhard's[7] method. Other experimental proceedures adopted were similar to those of Sinha and Prasad[8]. The temperature of the thermostat was kept constant within ±0.05°. Duplicate cells were set up in each case and readings were taken at an interval of one hour after the equilibrium had been established. The readings generally agreed within 0.1mV though in a few cases it went up to 0.15 mV. These mean of four e.m.f values along with the

TABLE 1

Temperature 5°

Mixture of $ZnBr_2$ & HBr $[ZnBr_2]_T$	$[HBr]_T$	E in volt	$[Zn^{++}] \times 10^3$	$[Br^-] \times 10^3$	$[ZnBr^+] \times 10^3$	$\mu \times 10^3$
0.008	0.004	0.40060	6.77	18.77	1.23	25.54
0.012	0.006	0.41978	11.23	29.23	0.77	40.46
0.016	0.008	0.43283	14.94	38.94	1.06	53.88
0.020	0.010	0.44283	18.30	48.30	1.70	66.60
0.022	0.011	0.44714	20.04	53.04	1.96	73.08
0.024	0.012	0.45106	21.70	57.70	2.30	79.40
0.026	0.013	0.45467	23.34	62.34	2.66	85.68
0.028	0.014	0.45802	24.98	66.98	3.02	91.96

TABLE 2

Temperature 15°

Mixture of $ZnBr_2$ & HBr $[ZnBr_2]_T$	$[HBr]_T$	E in volt	$[Zn^{++}] \times 10^3$	$[Br^-] \times 10^3$	$[ZnBr^+] \times 10^3$	$\mu \times 10^3$
0.008	0.004	0.38891	7.00	19.00	1.00	26.00
0.012	0.006	0.40809	10.68	28.68	1.32	39.36
0.016	0.008	0.42121	13.54	37.54	2.46	51.08
0.020	0.010	0.43162	16.76	46.76	3.24	63.52
0.022	0.011	0.43608	18.37	51.37	3.63	69.74
0.024	0.012	0.44030	20.35	56.35	3.65	76.70
0.026	0.013	0.44404	21.92	60.92	4.08	82.84
0.028	0.014	0.44751	23.49	65.49	4.51	88.98

TABLE 3

Temperature 25°

Mixture of $ZnBr_2$ & HBr $[ZnBr_2]_T$	$[HBr]_T$	E in volt	$[Zn^{++}]$ $\times 10^3$	$[Br^-]$ $\times 10^3$	$[ZnBr^+]$ $\times 10^3$	$\mu \times 10^3$
0.012	0.006	0.39734	11.10	29.10	0.90	40.20
0.016	0.008	0.41130	14.84	38 84	1.16	53.68
0.020	0.010	0.42217	18.66	48.66	1.34	67.32
0 022	0 011	0.42677	20.45	53.45	1.55	73.90
0.024	0.012	0.43101	22.32	58.32	1.68	80.64
0.026	0.013	0.43498	24.37	63.37	1.63	87.74
0.028	0.014	0.43861	26.28	68.28	1.72	94.56

TABLE 4

Temperature 35°

Mixture of $ZnBr_2$ & HBr $[ZnBr_2]_T$	$[HBr]_T$	E in volt	$[Zn^{++}]$ $\times 10^3$	$[Br^-]$ $\times 10^3$	$[ZnBr^+]$ $\times 10^3$	$\mu \times 10^3$
0.008	0.004	0.36631	6.65	18.65	1.35	25.30
0.012	0.006	0.38650	9.84	27.84	2.16	37.68
0.020	0.010	0.41197	16.29	46.29	3.71	62.58
0.022	0.011	0.41685	18.18	51.18	3.82	69.36
0.024	0.012	0.42122	19.86	55.86	4.14	75.72
0.026	0.013	0.42533	21.78	60.78	4.22	82.56
0.028	0.014	0.42882	22.77	64.77	5.23	87.54
0.030	0.015	0.43260	25.36	70.36	4.64	9 5.72

concentration of various ions are given in Tables 1 to 4. The symbol $[\ ]_T$ represents the stoichiometric concentrations in gm moles/litre. The ionic strength in no case exceeded 0.1.

Discussion

The e.m.f. of the cell,

$$Ag \left| AgBr \begin{array}{c} HBr\ (c_1) \\ ZnBr_2(c_2) \end{array} \right| \begin{array}{c} HBr\ (c_1) \\ ZnBr_2(c_2) \end{array} \left| \begin{array}{c} HBr\ (c_1) \\ ZnBr_2(c_2) \end{array} \right| Q.H. \Big| \ Pt,$$

is given by the equation,

$$E = E^\circ + \frac{2.30259RT}{F} \log [H^+][Br^-] f H f Br \qquad (1)$$

and the activity coefficient product is given by the expression,

$$-\log f H f Br = \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} - B\mu \qquad (2)$$

where 'A'[9] is the constant of Debye – Hückel equation and B is found from the study of cell reported earlier[10]. The values of 'A' and 'B' at various temperatures are given below :

	5°	15°	25°	35°
A	0.4921	0.5002	0.5092	0.5190
B	0.5618	0.5476	0.5274	0.5152

Assuming that the first stage of dissociation, $ZnBr_2 = Zn^{++} + Br^-$ is complete in very dilute solutions, the only ions present in these solutions can be Zn^{++}, $ZnBr^+$, Br^- and H^+, and hence the ionic strength of the solution will be given by the equation,

$$\mu = 2[Zn^{++}] + \tfrac{1}{2}[ZnBr^+] + \tfrac{1}{2}[H^+] + \tfrac{1}{2}[Br^-] \qquad (3)$$

So far $[H^+]$ is concerned, it is evidently equal to $[HBr]_T$. For finding the value of other concentration terms, an arbitrary value is given to the ionic strength μ. The corresponding value of $f H^+ f Br^-$ is calculated from equation (2), there after that of $[Br^-]$ from equation (1), that of $[ZnBr^+]$ from the relationship, $[Br^-] + [ZnBr^+] = 2[ZnBr_2]_T + [HBr]_T$, and that of $[Zn^{++}]$ from the relationship, $[ZnBr_2]_T = [Zn^{++}] + [ZnBr^+]$. With the values of $[H^+]$, $[Br^-]$, $[ZnBr^+]$ and $[Zn^{++}]$ thus found, a new value of μ is obtained. This process is repeated till μ becomes constant up to the fifth place of decimal. These final values of $[Zn^{++}]$, $[ZnBr^+]$ and $[Br^-]$ corresponding to the constant value of μ represent the correct values of concentrations and they are given in the Tables.

The dissociation constant (K_2) of $ZnBr^+$ is given by,

$$K_2 = \frac{[Zn^{++}][Br^-]}{[ZnBr^+]} \times \frac{f Zn f Br}{f ZnBr} = K_{A(2)} \frac{f Zn f Br}{f ZnBr}$$

Applying the equation, $-\log f i = \frac{AZi^2\sqrt{\mu}}{1+\sqrt{\mu}} - B_i\mu$,

we get, $$\log K_{A(2)} - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_2 - B\mu \qquad (4)$$

The value of $K_{A(2)}$ is next calculated from the values of $[Zn^{++}]$, $[Br^-]$ and $[ZnBr^+]$ determined, as explained earlier. The left hand side of the equation (4) is plotted against μ and the value of $\log K_2$ is obtained from the intercept of the straight line corresponding to $\mu = 0$.

The values of K and B_1 at various temperatures are given below :

	5°	15°	25°	35°
$K \times 10^2$	25.59	5.73	9.73	3.39
B_1	+1.330	−3.648	−5.916	−5.984

It may be pointed out here that several similar measurements have been made in this laboratory by Prasad and his co-workers. And in no case the value of B has been found to be reversed, which we have found in case of zinc bromide at 5°. This value of B at ' ° was checked and was found to be the same. We have not found the reason for this positive value of B at 5°, though such deviations have been found to occur in case of viscosity measurements $\left(\frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC\right)$ at lower temperatures in case of some salts. The value of Heat content change $\triangle H$ for the reaction $ZnBr^+ \rightleftharpoons Zn^{++} + Br^-$, has been calculated by plotting log K against $\frac{1}{T}$ and it comes out to be 1331 ± 100 cals/mole. And the values of $\triangle G^\circ$ and $\triangle S^\circ$ at 25° are respectively -5.482 and 4.486.

Acknowledgement

One of the authors (H.K.S.) is thankful to the Bihar State University Commission, for the award of a fellowship during the period this work was done. Thanks are also due to the authorities of Patna University for the laboratory and library facilities.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 1002-1005

Structure of the Degraded *Anacardium occidentale* (Cashew Nut Tree) Gum

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Manuscript received 10 April 1978, revised 3 June 1980, accepted 26 July 1980

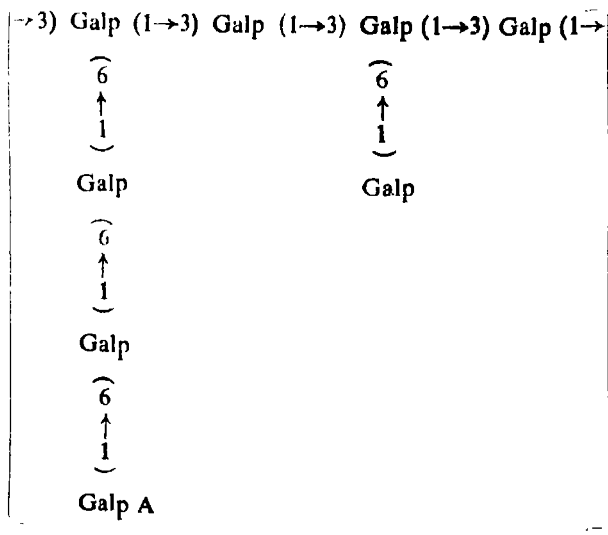
The structure of the degraded *Anacardium occidentale* gum has been deduced from the results of methylation, periodate oxidation and Smith degradation experiments Completely methylated degraded gum upon acid hydrolysis produced 2,3,4,6-tetra-, 2,4,6-tri-, 2,3,4,-tri- and 2,4 di O-methyl-D-galactose and 2,3,4-tri O-methyl-D-galacturonic acid in a molar ratio of 1.2·2:2·1. This shows the branched chain nature of the degraded gum and its repeating unit consists of a 1→3 linked galactan main chain to which are attached two side chains of galactose and aldobiouronic acid by 1→6 linkages. The results of periodate oxidation and Smith degradation confirm the above structure. The molecular weight determination shows that the repeating unit is repeated seventeen times in the full structure of the degraded *A. occidentale* gum

It has been reported earlier[1] that the water soluble *Anacardium occidentale* gum is composed of D-galactose, L-arabinose and D-galacturonic acid residues, the two sugars galactose and arabinose being present in a molar proportion of 17:1. Autohydrolysis of the gum generates a degraded gum which on graded hydrolysis gives rise to an aldobiouronic acid, 6-O-(β-D-galactopyranosyl uronic acid)-D-galactose along with galactose. The present communication deals with the structure of the degraded gum which has been arrived at from the results of methylation, periodate oxidation and Smith degradation reactions.

Pure degraded gum has an Eq. Wt. 1327, Mol. Wt. 23250 and D.P. value 17. The IR spectrum of the compound, besides indicating the presence of -OH (3333 cm^{-1}) and COO^- (1602 & 1270 cm^{-1}) carries two weak absorption bands at 890 (hump) and 780 cm^{-1} suggestive of a β-linkage. Complete acid hydrolysis shows that degraded gum is composed of galactose and galacturonic acid in a molar proportion of 7:1. The degraded gum was fully methylated using Haworth's method[2] followed by Purdie's method[3]. The product showing absence of -OH band in IR spectrum was hydrolysed and the acidic methyl sugar was separated from neutral ones. The former sugar was identified as 2,3,4-tri-O-methyl-D-galacturonic acid as described earlier[1]. The neutral methylated sugar mixture was found to contain 2,3,4,6-tetra-, 2,4,6-tri-, 2,3,4-tri- and 2,4,-di-O-methyl-D-galactose in a molar ratio of 1:2:2:2. The mixture was separated on thick filter papers and the individual methyl sugars were identified through their R_G values, rotations and characteristic crystalline derivatives.

In each repeating unit of the degraded gum, there are two non-reducing end groups, one occupied by D-galactopyranose and the other by D-galacturonic acid units. Two 1→3 linked and two 1→6 linked galactose units are also present in each repeating unit. Of the two 1→6 linked galactose residues, one is a part of aldobiouronic acid and the other serves as a link between 1→3 linked galactan backbone and the aldobiouronic acid side chain. At the branch point, the galactose moiety is linked through C_1, C_3 and C_6 and there are two such residues in a repeating unit. To accommodate all the types of linkages present, the following tentative structure.

(I) has been proposed for the repeating unit of the degraded *A. occidentale* gum.



(I)

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(Galp=D-Galactopyranose and GalpA=D-Galactopyranosyl uronic acid).

In (I), the glycosidic bonds have been assigned β-configuration since the IR spectra of both degraded gum and its permethylated product show absorption bands in the region of 891 ± 7 cm^{-1} which may be ascribed[4] to a linkage of β-type. The cross reaction of the gum[1] with anti-Pn-VII serum supports the existence of β-linkages[5].

Upon oxidation with sodium metaperiodate degraded gum consumed 0.99 moles of oxidant with simultaneous liberation of 0.49 moles of formic acid per anhydrohexose unit These data are in agreement with the structure (I). Hydrolysis of the periodate oxidised gum liberated galactose residues (4 moles) which had survived oxidation Finally the polyaldehyde formed as a result of periodate oxidation of the degraded gum was subjected to reduction with sodium borohydride followed by hydrolysis with acid[6]. Paper chromatographic analysis of the hydrolyzate showed the presence of galactose, glycerol and glycolaldehyde. A quantitative estimation revealed that galactose and glycerol were present in a molar proportion of 1:0.98. These results are comparable with the theoretical values expected from the proposed structure (I). Since D.P. of the polysaccharide is 17, the repeating unit occurs seventeen times in the full structure of degraded gum. It might be mentioned here that the structures of the degraded. *A. occidentale* gum and degraded *A. occidentale* shell polysaccharide[7] differ due to slight variation in the arrangement of galactose residues in the main as well as side chain.

Experimental

Paper chromatograms were run by the descending method on Whatman No. 1 and 3 mm filter papers with the following solvent mixtures : (S_1) butan-1-ol-ethanol-water (1:1:4, upper phase), (S_2) Butan-1-ol-acetic acid-water 4:1:5, and (S_3) 2-butanone-water azeotrope[8]. Spray reagents used are (R_1) *p*-anisidine phosphate, (R_2) ethanolic solution of aniline (1%) and trichloroacetic acid(5%) and (R_3) sodium metaperiodate and benzidine B.[9] Rg values are with reference to 2,3,4,6-tetra-O-methyl-D-glucose. Evaporations were carried out at 45-50° under reduced pressure. Specific rotations are equilibrium values and the m.p.s. are uncorrected. IR spectrum was taken with a Perkin Elmer Infracord spectrophotometer, model 137-B.

Degraded A. occidentale gum : *A. occidentale* gum (20 g) was heated with water (500 ml) on a steam bath for 90 hr when the autohydrolysis was complete (as revealed from kinetic studies). The autohydrolyzate was cooled, neutralized (barium hydroxide) and filtered. The filtrate, after concentration to 100 ml, was dialyzed against distilled water for 48 hr. The dialysed solution was made alkaline (*p*H 8.0) by addition of baryta solution and concentrated. The syrup on treatment with hot dry methanol furnished degraded *A. occidentale* gum as a light yellow powder. This was further purified by refluxing with dry methanol (yield 14 g) (Found Ba, 4.93% ; Eq. Wt. 1327). The IR spectrum showed absorption bands at 3333, 1602, 1370, 1143 1075, 890 (bump) and 780 cm^{-1}. From the values of sedimentation constant (S^{20}, 1.866×10^{-13}), diffusion coefficient (D^{20}, 5.305×10^{-7}) and partial specific volume at 20° (δ, 0.63), the molecular weight of the degraded gum has been calculated to be 23250.

Hydrolysis of the degraded gum : Degraded gum (0.21g) was hydrolysed with sulphuric acid (IN, 20 ml) in a sealed tube for 20 hr. The seal was broken and the hydrolyzate was worked up in the usual manner to obtain a syrup which on paper chromatographic examination (solvent S_1, spray reagent R_1) furnished only two spots corresponding to D-galactose and D-galacturonic acid. A quantitative estimation[10] of the individual components showed the presence of galactose and galacturonic acid in a molar ratio of 7:1.

Methylation of the degraded gum : To a solution of the degraded gum (30 g) in aqueous sodium hydroxide (300 ml, 30%) was added dropwise neutral dimethyl sulphate 200 ml) during a period of 6 hr. with constant stirring and the temperature of the reaction mixture was maintained at 10°. After allowing the reaction to continue at room temperature for 6 hr. the solution was neutralized (*p*H 7.0) with sulphuric acid and concentrated to half its volume when a semi-solid mass (A) floated up which was removed and kept. Crystals of sodium sulphate which separated out after cooling the concentrate was extracted with methanol. The methanolic concentrate was mixed with the aqueous filtrate and evaporated to a syrup. The combined mixture of the syrup and semi-solid mass (A) was remethylated with sodium hydroxide (100 ml) and dimethylsulphate (50 ml). The reaction product, after being worked up, was extracted with chloroform in a liquid-liquid extractor at *p*H 8.0 for 10 hr. The aqueous layer was acidified (*p*H 2.0) and extracted exhaustively with chloroform. The dark red chloroform extract was concentrated to yield a partially methylated compound (20.4 g). This was further methylated twice by Purdie's method by treating with methyl iodide (80 ml) and freshly prepared silver oxide (16 g). Finally, a light yellow syrupy liquid was obtained (yield, 18.2 g ; Found : OCH_3, 41.98%). The I.R. spectrum of the compound showed absence of absorption band for – OH but contained other absorption bands at 1739, 890 and 765 cm^{-1}.

Hydrolysis of the methylated degraded gum : The methylated degraded gum (7.8 g) was hydrolysed[11] with cold 72% sulphuric acid (50 ml) at room temperature for 1 hr. The solution was then diluted with water to reduce the acid concentration to 12% and was heated on a steam bath for 4 hr. It was cooled, neutralized (barium carbonate) and concentrated to a thin syrup. This was made alkaline (*p*H 8.0), saturated with sodium chloride and extracted with ethyl acetate in a liquid-liquid extractor for 10 hr to obtain the neutral methylated sugars (5.01 g). The aqueous layer, after

being acidified (pH 2 0) was extracted with ethyl acetate in the same way to obtain methylated uronic acid moiety (0 68 g). Upon paper chromatography, it gave an intense red spot (Rg 0.62 in solvent S_2, spray reagent R_2) corresponding to 2,3,4-tri-O-methyl-D-galacturonic acid. The acidic sugar was finally identified as 2:3:4:-tri-O-methyl-D-galacturonic acid as reported earlier[1].

The neutral methylated sugars were found to be a mixture of four components as revealed from its paper chromatograms run in two different solvents S_1 and S_2 (Spray reagent R_1). Resolution of this mixture into its components was conducted by preparative partition chromatography on Whatman No. 3 M filter paper sheets (solvent S_1). The strips corresponding to individual methylated sugars were eluted with water and eluates were identified as follows :—

Fraction I : 2, 3, 4, 6-tetra O-methyl-D-galactose-Syrup (0.145 g, Rg 0 [illegible]9 in S_1), $(\alpha)_D^{30} + 114°$ (c, 1.1 in water) furnished a cyrstalline anilide, m.p. and m.m p., 190°.

Fraction II : 2, 4, 6 tri-O-methyl-D-galactose-Syrup (0.303 g, Rg 0 67 in S_1), $(\alpha)_D^{30} + 92°$ (c, 1.4 in water) furnished a crystalline 2,4,6-tri-O-methyl-N-phenyl-D-galactosylamine, m.p: and m.m.p., 177-78°.

Fraction III : 2,3,4-tri-O-methyl D-galactose-Syrup (0.298 g, Rg 0.65 in S_1), $(\alpha)_D^{30} + 142°$ (c, 1.2 in water) was converted into its crystalline anilide derivative, m.p. and m.m.p., 165 66°.

Fraction IV : 2, 4-di-O-methyl-D-galactose Syrup (0.262 g., Rg 0 40 in S_1), $(\alpha)_D^{30} + 86°$ (c, 1.05 in water) crystallised from ethyl acetate in the form of needles, m.p. 103-104° (lit.[12], m p., 103°). It gave a crystalline 2,4-di-O-methyl-N-phenyl-D-galactosylamine, m.p. and m.m.p. 216-17°.

A quantitative estimation of the methylated sugars by the hypoiodite oxidation method[13] showed that 2,3,4,6-tetra-, 2,4,6-tri-, 2,3,4-tri, and 2,4-di-O-methyl-D-galactoses were present in a molar ratio of 1:2:2:2.

Periodate oxidation of the degraded gum : An aqueous solution of the degraded gum (0.2054 g) was treated with sodium metaperiodate solution (0.15 *M*, 25 ml) and the volume was made up to 250 ml with water. It was kept in the dark at room temperature for 7 days. A blank experiment was set up in the same manner with the same volume of 0.15 *M* sodium metaperiodate solution. Aliquots (5 ml each) were removed from both the solutions at regular intervals to determine the amount of periodate consumed and formic acid liberated.

The formic acid produced and periodate consumed at the final stage were observed to be 0.49 and 0.99 moles per anhydrohexose unit respectively.

Hydrolysis of the periodate oxidised degraded gum : An aqueous solution of the periodate oxidised degraded gum was treated with ethylene glycol to destroy excess of periodate and the inorganic ions were eliminated by dialysis. The dialysed solution was evaporated to a syrup and hydrolysed by heating with *N* sulphuric acid (10 ml) for 4 hr. The hydrolyzate after being worked up showed the presence of D-galactose when examined paper chromatographically. A quantitative estimation of the sugar in the hydrolyzate showed the presence of 3.89 moles of galactose per equivalent of the degraded gum.

Smith degradation of the degraded gum : The degraded gum (0.1858 g) was oxidised with sodium metaperiodate for 48 hr at room temperature until the periodate consumption became constant. Excess oxidant was removed by adding ethylene glycol and the solution was dialysed against running distilled water till it was free from inorganic ions. The dialysed polyaldehyde solution was treated with sodium borohydride (0.25 g) for 24 hours. After removal of excess borohydride by aqueous acetic acid (1:1), the solution was evaporated to dryness. The borate ions were removed as methyl borate and the borate free product was hydrolyzed with sulphuric acid (1*N*, 10ml) for [illegible] hr. The hydrolyzate, after being worked up, was evaporated to a thin syrup. This, on paper chromatographic examination (solvent S_1, reagent R_3) gave three spots corresponding to galactose, glycerol and glycolaldehyde. A part of the syrup was resolved into its components on Whatman No. 3 mm sheets. The zones corresponding to galactose and glycerol were eluted with water and individual components were estimated by phenol-sulphuric acid[14] and chromotrophic acid[15] reagents respectively. Galactose and glycerol were found to be present in a molar ratio of 1:0 98.

Acknowledgement

The authors express their sincere thanks to Professor J. Rosik', Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Czechoslovakia for his generous help in determining the diffusion coefficient and sedimentation constant of the degraded gum and to Dr. N.A. Ramaiah, Director, for his kind interest in this investigation.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 1006-1010

Synthesis of Some New 2-Aryloxymethyl-Δ^2-1,3,4-oxadiazolin-5-ones and Their Related Compounds as Potential Pesticides

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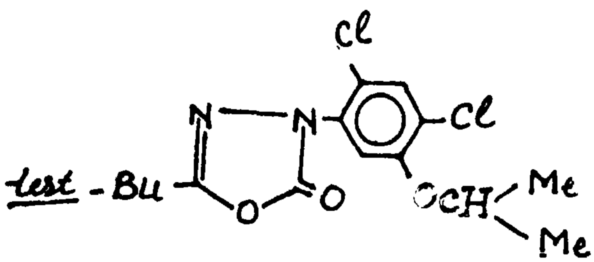
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Manuscript received 3 January 1980, revised 3 June 1980, accepted 26 July 1980

2-aryloxymethyl-Δ^2-1,3,4-oxadiazolin-5-ones (II) obtained by cyclisation of N-aryloxyacetyl ureas (I) with Br_2/NaOH were treated with aryloxyacetyl chloride, and NH_4SCN/benzoyl chloride to yield 4-aryloxyacetyl-2-aryloxy methyl-Δ^2-1,3,4-oxadiazolin-5-ones (III) and 2-aryloxymethyl-4-(N-benzoylthioamido)-Δ^2-1,3,4-oxadiazolin-5-ones (IV), respectively. The 1,3,4-oxadiazolinone (II) on treatment with NH_4OH/CS_2 yielded 2-aryloxymethyl-5-oxo-Δ^2-1,3,4-oxadiazoline-4-dithiocarboxylic acids (V), which when refluxed with I_2/EtOH afforded *bis* (2-aryloxymethyl-5-oxo-Δ^2-1,3,4-oxadiazoline-4-thiocarbonyl)disulphides (VI). Out of thirteen screened compounds, two exhibited herbicidal activity in the range of 2,4-D (sodium salt), a commercial herbicide, against *Argemone mexicana* and *Cyperus rotundus*, and three showed fungitoxicity of the order of Dithane M-45 (Manganous ethylenebisdithiocarbamate with zinc ion), a commercial fungicide, against *Aspergillus niger* and *Helminthosporium oryzae*.

THE novel exploration of *oxadiazon* (G-315), the 2-*tert*-butyl-4-(2, 4-dichloro-5-*iso*-propoxyphenyl)-Δ^2-1,3,4-oxadiazoline-5-one (1) which is a broad spectrum commercial herbicide recommended for application on various crops and ornamental plants, has been an incentive for investigations in the field of 1,3,4-oxadiazole herbicides. Further, various phenolic ethers[1-4], 2-substituted-Δ^2-1, 3, 4-oxadiazolin-5-ones[5-9], amides[10] and thioureas[11-18] have been reported as useful biologically active compounds especially as herbicides and fungicides.



(1)

In view of above, it was speculated that the combination of *oxadiazon* with the moieties responsible for biological activity might result in compounds with better performance.

In addition to the fact that a number of heteroaryl disulphides have been reported as useful bactericides, fungicides, acaricides and herbicides, one might expect that the disulphides with biologically versatile 1,3,4-oxadiazole nucleus would be compounds of high potency.

Considering these facts in view, the title compounds have been synthesised to study their herbicidal and fungicidal activities.

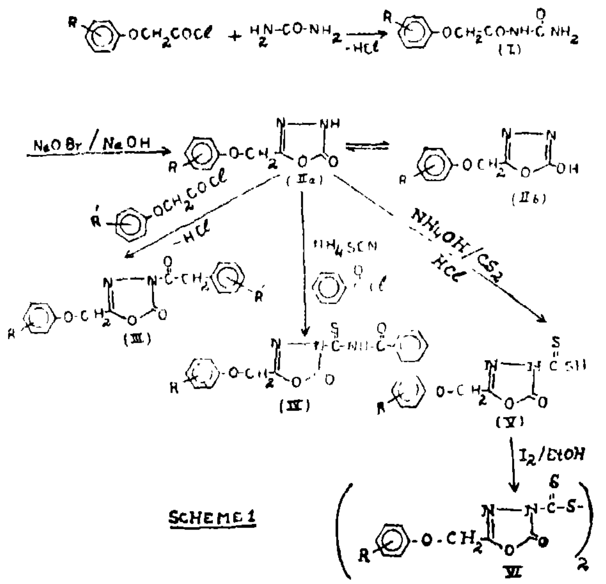
The title compounds have been synthesised according to the scheme 1.

The 2-aryloxymethyl-Δ^2-1,3,4-oxadiazolin-5-ones(II) prepared by cyclisation[23] of N-aryloxyacetylureas (0.1M) with an ice-cold solution of Br_2/NaOH (2N) in 80-85% yield were stirred with aryloxyacetyl chloride for 30 min in an ice bath followed by washing with Na_2CO_3 solution to yield 4-aryloxyacetyl-2-aryloxymethyl-Δ^2-1, 3, 4-oxadiazolin-5-ones (III) in 85-89% yield. The 2-aryloxymethyl-4-(N-benzoylthioamido)-Δ^2-1,3,4-oxadiazolin-5-ones (IV) with 90-95% yield, were prepared according to the method of Doughlass and Dains[24] by refluxing (II) with NH_4SCN/benzoyl chloride in acetone for 2 hr. (V) were prepared in good yield (81-85%) by stirring a mixture of (II) 0.05M, Ammonia solution (sp.gr. 0.88) and CS_2 for 2 hr at

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room temperature followed by acidification with dil. HCl, which on refluxing with I_2/EtOH, furnished bis (2-aryloxymethyl-5-oxo-Δ^2-1, 3, 4-oxadiazoline-4-thiocarbonyl) disulphides (VI) in 90-95% yield. The compounds thus prepared were characterised by their m.ps., elemental analyses, ir and NMR spectra.



SCHEME 1

Thirteen of the title compounds have been screened for their herbicidal activity against the weeds *Argemone mexicana*[19] and *Cyperus rotundus*[19] and fungi *Aspergillus niger*[20] and *Helminthosporium oryzae*[21]. The results obtained have been compared with *2,4-D*, a commercial herbicide and *Dithane M-45*, a commercial fungicide which were tested under the similar conditions. Out of the thirteen tested compounds, two exhibited herbicidal activity in the range of 2,4-D and three showed fungitoxicity of the order *Dithane M-45* at concentrations 1000 ppm and 100 ppm. However, the bis-oxo-oxadiazolinthiocarbonyl disulphides (VI) were found to be more active than 4-aryloxyacetyl-, and 4-(N-benzoylthiomido)-Δ^2-1, 3, 4-oxadiazolin-5-ones (III), (IV).

Experimental

The melting points are uncorrected. The ir spectra (in KBr) were recorded on Perkin-Elmer Spectrophotometer (model 521) and NMR on 60 MHZ spectrophotometer using TMS as internal standard. The chemical shifts are reported in τ(ppm) values.

N-aryloxyacetylureas (I) were prepared by the method of Pearl and Dehn[22].

2-Aryloxymethyl-Δ^2-1, 3, 4-oxadiazolin-5-ones(II)[23] : I (0 1*M*) was added portionwise with stirring to an ice-cold solution of NaOH (2*M*, 168 ml) and bromine (17.6g). The mixture was poured into water after 15 min to yield the oxadiazolinone (II) which were recrystallised from ethanol, and are recorded in Table 1A.

TABLE 1A—2-ARYLOXYMETHYL-Δ^2-1,3,4-OXADIAZOLIN-5-ONES(II)

S.No.	R	M.P. °C	Yield %
1[a]	H	164	85
2[b]	*o*-Cl	165-166	80
3	*p*-Cl	199-201	82
4	2,4-Dichloro	160	75
5	*m*-CH_3	169	76

Significant bands (cm^{-1}) in ir spectra (in KBr)

	C=N	C–O–C	*C=O	N–H	Substituted benzene nucleus
a	1615	1260,1040	1715	3440,3140	1500,770,710
b	1615	1020,1250	1710	3440,3160	1510,1470,730

*The cyclic C=O band (1710-1715 cm^{-1}) was present in the compounds (II), confirming their existence as mainly in the oxo form instead of the tautomeric hydroxy form (IIa).

TABLE 1B—4-ARYLOXYACETYL-2-ARYLOXYMETHYL-Δ^2-1,3,4-OXADIAZOLIN-5-ONES (III)

S.No.	R	R′	M.P. °C	Yield %
6	H	*p*-Cl	173-174	81
7	H	2,4-Dichloro	156	89
8	H	*m*-CH_3	163	74
9[a]	*o*-Cl	2,4-Dichloro	99-101	85
10	*o*-Cl	*o*-Cl	158	80
11	*o*-Cl	*p*-Cl	160-161	70
12	*p*-Cl	*o*-Cl	184-185	72
13	*p*-Cl	*p*-Cl	138	84
14	*p*-Cl	2,4-Dichloro	180	86
15	*p*-Cl	*m*-CH_3	162	87
16	2,4-Dichloro	2,4-Dichloro	105-107	73
17	2,4-Dichloro	*m*-CH_3	169	74
18	2,4-Dichloro	*p*-Cl	186	76
19	*m*-CH_3	*p*-Cl	170-171	79
20	*m*-CH_3	2,4-Dichloro	176	68

Significant bands (cm^{-1}) in ir Spectra (in KBr)

	C=N	C=O (Cyclic)	C=O (Acyclic)	C–O–C	Substituted benzene nucleus
a	1615	1715	1630	1040 1260	1490, 880, 800, 760
b	1630	1720	1640	1030 1260	1500, 1450, 880, 820

TABLE 1C—2-ARYLOXYMETHYL-4-(N-BENZOYLTHIOAMIDO)-Δ^2-1,3,4-OXADIAZOLIN-5-ONES (IV)

S.No.	R	M.P. °C	Yield %
21	H	155	85
22	o-Cl	133	88
23	p-Cl	160	90
24[a]	2,4-Dichloro	141	92
25	m-CH_3	159	95

Significant bands (cm^{-1}) in ir spectra (in Nujol mull)

	C=N	C-O-C	C=O (Cyclic)	C=O (Acyclic)	C=S	N-H	Substituted benzene nucleus
a	1630	1050, 1260	1740	1700	1220	3300 3070	1560,1485, 805,730

NMR spectrum in DMSO-d_6 (60 MHZ)

	Protons	Chemical shift (τ)	Multiplicity
a	Aromatic (8H)	1.9 – 2.5	Complex multiplet
	$-OCH_2$ (2H)	5.1	Singlet
	–NH (H)	6 6	Singlet

TABLE 1D—2-ARYLOXYMETHYL-5-OXO-Δ^2-1,3,4-OXADIAZOLIN-4-DITHIOCARBOXYLIC ACIDS

S.No.	R	M.P. °C	Yield %
26	H	180-182	80
27	o-Cl	230	82
28	p-Cl	215	95
29	2,4-Dichloro	195-198	76
30[a]	m-CH_3	130-135	80

BIS (2-ARYLOXYMETHYL-5-OXO-Δ^2-1,3,4-OXADIAZOLIN-4-THIOCARBONYL) DISULPHIDES

S.No.	R	M.P. °C	Yield %
31	H	232-235	75
32	o-Cl	200	80
33	p-Cl	185	90
34	2,4-Dichloro	172-175	95
35[b]	m-CH_3	220-225	95

Significant bands (cm^{-1}) in ir spectra (in KBr)

	C=N	C=O	C-O-C	C=S	S-H	Substituted benzene nucleus
a	1622	1730	1040,1260	1120	2560	1520,780,700
b	1650	1260 1045	1710	1220	—	1580,1500,800,680

C, H and N analysis of compound given in Table 1A and 1B and N, S, analysis of compound given in Table 1C and 1D are consistent.

4-Aryloxyacetyl-2-aryloxymethyl-Δ^2-1, 3, 4-oxadiazolin-5-ones(III): A mixture of oxadiazolinone (II, 0.02 *M*) and aryloxyacetyl chloride (0.02 *M*) was stirred for about 30 min in an ice-bath and then cold water was added. The product thus precipitated was filtered, washed several times with Na_2CO_3 solution and recrystallised from ethanol. The compounds (III) are recorded in Table 1B.

2-Aryloxymethyl-4 (N-benzoylthioamido)-1, 3, 4-Δ^2-oxadiazolin-5-ones (IV)[24] : Were prepared by reacting equimolar quantities of (II) NH_4SCN and benzoyl chloride in acetone following the method of Douglass and Dains[24]. The compounds (IV) thus prepared were recrystallised from acetone-ethanol mixture, and are recorded in Table 1C.

2-Aryloxymethyl-5-oxo-Δ^2-1,3,4-oxadiazolin-4 dithiocarboxylic acids (V). To a mixture of 2-aryloxymethyl-Δ^2-1, 3, 4-oxadiazolin-5-ones (II, 0.05*M*) and ammonia solution (15 ml, sp.gr. 0.88), CS_2 (0.005 *M*) was added dropwise. After stirring the reaction mixture for 2 hr. at room temperature it was acidified with dil. HCl to give the corresponding dithiocarboxylic acids which were recrystallised from aqueous-ethanol (20 80 ; v/v) as white crystals and are recorded in Table 1D.

Bis (2-aryloxymethyl-5-oxo-Δ^2-1, 3, 4 oxadiazolin-4-thiocarbonyl) disulphides VI : To an ethanolic suspension of 2-aryloxymethyl-5-oxo-Δ^2-1,3,4-oxadiazolin-4-dithiocarboxylic acid (V), ethanolic solution of I_2 was added until no further decolorisation of I_2 was observed. The mixture was heated on water bath for 15 min, cooled and poured into water followed by basification with aq. ammonia to yield the disulphides (VI) which were recrystallised from ethanol and are recorded in Table 1D.

Herbicidal Screening

Herbicidal activity was evaluated by pre-emergence test at three concentrations viz. 1000, 100 and 10 ppm against *Argemone mexicana* and *Cyperus rotundus*. The number of replications in each case was three. Seeds/tubers of the test plants were soaked for 24 hr. in the test solutions and then planted. *2,4-D* (sodium salt) was also tested under similar conditions (with a view to comparing the results). The percentage inhibition by various compounds are recorded in Table 2.

$$\% \text{ Inhibition} = \frac{Gc - Gt}{Gc} \times 100$$

where, Gc = No. of germinated seeds/tubers in control.

Gt = No. of germinated seeds/tubers in test solution/suspension.

TABLE 2 – HERBICIDAL SCREENING

Compound serial as in Tables 1A, 1B, 1C and 1D	Average Percentage Inhibition					
	Weed-*A. mexicana* Concentrations used			Weed-*C. rotundus* Concentrations used		
	1000ppm	100ppm	10ppm	1000ppm	100ppm	10ppm
1	60.5	33.2	24.4	53.6	21.6	13.5
3	62.7	35.7	26.1	56.8	23.0	14.9
4	66.0	37.3	28.2	68.4	36.9	18.3
5	64.7	35.9	26.5	65.3	25.6	16.5
6	68.4	39.0	31.5	68.1	39.4	26.6
7	71.5	40.1	34.0	69.4	31.3	29.7
13	66.1	39.4	28.1	60.3	30 4	20.8
14	95.4	56.9	27.2	94.8	56.2	28.2
21	96.3	58.5	28.4	95.7	57.3	28.9
24	97.9	61.1	30.4	96.4	58.5	30 1
31	72.5	40.2	15.5	55.1	41.4	19.7
33	63.4	37.0	27.7	58.2	25.2	16.8
34	85.2	48.3	22 8	79.5	40.6	18.9
2,4-D (Sodium salt)	100	84.2	66.7	100	82.6	61.5

TABLE 3 – FUNGICIDAL SCREENING

Compound serial as in Tables 1A, 1B, 1C and 1D	Average Percentage Inhibition after 96 hours					
	Organism-*A. niger* Concentrations used			Organism *H. oryzae* Concentrations used		
	1000ppm	100ppm	10ppm	1000ppm	100ppm	10ppm
1	53.7	27.5	18.2	48.2	18.4	9.4
3	56.5	28.4	20.1	51.4	21.3	11.7
4	62.0	32.5	21.9	64.8	29.6	15.2
5	59.8	30.1	21.2	58.1	22.3	13.7
6	66.1	34.3	22.4	65.0	30.1	18.6
7	68.3	39.2	23.0	69.9	38.4	20.5
13	64.4	31.4	18.3	61.4	23.6	17.5
14	95.9	56.3	31.4	94.6	54.7	28.1
21	96.7	60.1	36.3	95.5	61.8	50.2
24	100	65.5	60.8	100	70.4	55.7
31	98.4	62.8	40.1	97.2	63.0	51.2
33	100	68.6	52.2	100	70.2	53.1
34	100	72.3	55.0	100	74.4	54.3
Dithane M-45 (a commercial fungicide)	100	85.4	72.6	96.4	82.9	68.3

Fungicidal screening

The antifungal activity was evaluated by agar-plate technique[25] against *A. niger* and *H. oryzae* at 1000 ppm, 100 ppm and 10 ppm. The number of replications in each case was three. A commercial fungicide *Dithane M-45* was tested under similar conditions (with a view to comparing the results). The percentage inhibitions by various compounds are recorded in Table 3.

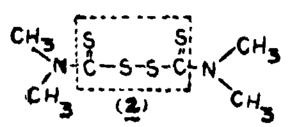
$$\% \text{ Inhibition} = \frac{(C - T) \times 100}{C}$$

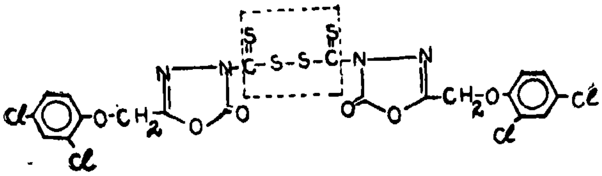
where, C = Diameter of fungus colony in control plates after 96 hours.

T = Diameter of fungus colony in treated plates after 96 hours.

Results and Discussion

It is evident from the screening data (Tables 2 and 3) that all the screened compounds were toxic to weeds (*A. mexicana* and *C. rotundus*) and fungi (*A. niger* and *H. oryzae*) in varied degrees, but the order of their toxicities was not so encouraging as could be expected from the combination of phenolic ether, oxadiazolinone and thiourea moieties. The compound Nos. 14 and 24 had the activity of the order of *2,4-D* (sodium salt) at 1000 ppm, presumably by virtue of possessing 2,4-dichlorophenoxy moiety which is common toxophore in the herbicides of *2,4-D* family. The compound Nos. 24, 33 and 34 inhibited >50% the growth of both the fungi even at 10 ppm, and thus appear to be promising fungicides. The compound No. 34 (3) was most active against both the fungal species, and had fungitoxicity of the order *Dithane M-45* (Mangeanous ethylenebis-dithiocarbamate with zinc ion) even at 100 ppm, it is only due to the S-S bond fission almost identical to that of thiram (2), a commercial fungicide, involving this bond fission in its mode of action[26].





(3)

However, the thioamido compound Nos. 21 and 24 were more toxic to both the weeds than their parent compounds, No. 1 and 4 as well as 4-aryloxyacetyl-Δ^2-1,3,4-oxadiazolin-5-ones Nos. 5, 6 and 14 respectively.

Acknowledgement

The authors express their sincere thanks to Prof. R. P. Rastogi, Head of the Chemistry Department, University of Gorakhpur, Gorakhpur, for providing departmental facilities and Dr A K. Singh (U.S.A) for recording ir, NMR spectra and elemental analyses. One of the authors (B. K. B.) is thankful to U.G.C., New Delhi for financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 1011-1013

Studies in the Synthesis of Xanthone Derivatives : Part II. Synthesis of Furoxanthones

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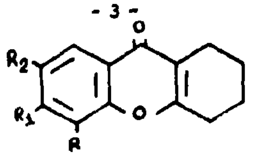
Manuscript received 24 September 1979, revised 19 June 1980, accepted 26 July 1980

7-Allyl-6-hydroxy-5-methyl-1,2,3,4-tetrahydroxanthone (Ia), on treatment with osmium tetroxide-potassium periodate, followed by cyclization with polyphosphoric acid afforded 5-methyl-1,2,3,4-tetrahydrofuro (2',3'-6,7) xanthone (II), which on dehydrogenation with palladised charcoal gave 4-methylfuro (3',2'-2,3) xanthone (III). It was also synthesised from 2-allyl-3-hydroxy-4-methylxanthone (IVa) by carrying out oxidation with osmium tetroxide-potassium periodate, and cyclization with PPA. Similarly furo (2',3'-3 4) xanthone (VI), was synthesised starting from 5-allyl-6-hydroxy-1,2,3,4-tetrahydroxanthone (Ic), and also from 4 allyl-3-hydroxyxanthone (IVb).

THE synthesis of furoxanthone, unsubstituted in furan ring was generally achieved by internal Claisen condensation[1] of the aldehydo ester derivative or by ozonolysis[2] of the *o*-hydroxyallylxanthone, followed by cyclization with polyphosphoric acid. Seshadri and coworkers[3] obtained *o*-hydroxyacetaldehydo derivatives, in good yield by oxidation with osmium tetroxide. We adopted the same method[3], for the synthesis, of two furoxanthones, viz. 4-methylfuro(3',2'-2,3)xanthone(III) and furo(2', 3'-3,4)xanthone[1] (VI), each was synthesised starting from two different types of *o*-hydroxyallylxanthones.

7-allyl-6-hydroxy-5-methyl-1, 2, 3, 4-tetrahydroxanthone(Ia), prepared as described in part-I[4] of the series, was subjected to oxidation with osmium tetroxide-potassium periodate in ethyl acetate-water to give corresponding 7-acetaldehydo derivative, which in next step cyclized to 5-methyl-1, 2, 3, 4-tetrahydrofuro-(2',3'-6,7) xanthone(II), with PPA. This on dehydrogenation with palladised charcoal (10%), in boiling diphenyl ether afforded 4-methylfuro(3', 2'-2, 3)xanthone(III). It was also synthesised, by the reaction of osmium tetroxide potassium-periodate on 2-allyl-3-hydroxy-4-methylxanthone (IVa), in ethyl acetate-water followed by cyclization of resulting intermediate with PPA.

- 3 -

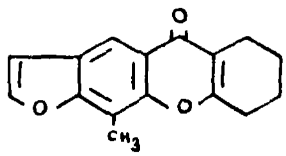


(Ia) R = CH_3, R_1 = OH, R_2 = $-CH_2-CH=CH_2$

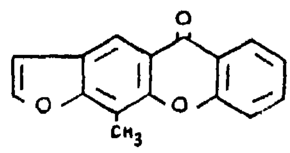
(Ib) R = CH_3, R_1 = OH, R_2 = $-CH_2-CHO$

(Ic) R = $-CH_2-CH=CH_2$, R_1 = OH, R_2 = H

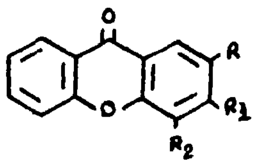
Similarly 5-allyl-6-hydroxy-1, 2, 3, 4-tetrahydroxanthone (Ic)[4] was converted to 1,2,3,4-tetrahydrofuro (3',2'-5,6)xanthone(V), by carrying out oxidation with osmium tetroxide-potassium periodate and cyclization with PPA. The compound(V), on dehydrogenation with palladised charcoal in boiling diphenyl ether gave furo-(2',3'-3,4)xanthone(VI). It was also synthesised from 4-allyl-3-hydroxyxanthone (IVb)[4], with the stepwise use of osmium tetroxide-potassium periodate and PPA.



(II)

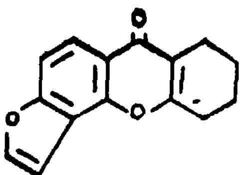


(III)

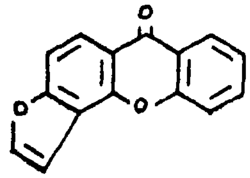


(IVa) R = $-CH_2-CH=CH_2$, R_1 = OH, R_2 = $-CH_3$

(IVb) R = H, R_1 = OH, R_2 = $-CH_2-CH=CH_2$



(V)



(VI)

Experimental

[1]H NMR spectra were recorded on Perkin Elmer R-32 90 MHz spectrometer using TMS as an internal standard. IR spectra were determined on a Beckmann IR-20 spectrophotometer. UV spectra were recorded on Beckmann DU-2 spectrophotometer.

7-Acetaldehydo 6-hydroxy-5-methyl-1, 2, 3, 4-tetrahydroxanthone(Ib) :

7-Allyl-6-hydroxy-5-methyl-1, 2, 3, 4-tetrahydroxanthone (0.8 g) in ethyl acetate (230 ml) and osmium tetroxide (70 mg) in water (80 ml) were vigorously stirred for 15 minutes. Potassium periodate (1.8 g) was added in small quantities to the dark solution over a period of 90 minutes. The reaction mixture was stirred 2 hr. more. The acetate layer was separated, washed with water, dried with sodium sulphate and concentrated. The residue left, was dissolved in chloroform and the clear solution was percolated through a short column of alumina. It was crystallised from acetic acid, m.p. 267°, yield 0.3g. Found. C, 70.71, H, 6.18. $C_{16}H_{16}O_4$ requires: C, 70.58, H, 5.88%). IR spectrum (nujol): 1630 cm^{-1} (γ-pyronyl>C=O), 1680 cm^{-1} (-CHO), and a broad band at 3350 cm^{-1} (-OH).

5-Methyl-1,2,3,4-tetrahydrofuro(2',3'-6,7)xanthone(II):

7-Acetaldehydo-6-hydroxy-5-methyl-1, 2, 3, 4-tetrahydroxanthone (0.25 g) was treated with PPA (12 ml) in an oil bath at 110° for 2 hr. It was then poured into ice water. The solid separated was filtered, washed with dilute sodium hydroxide solution and finally with water. It crystallised from benzene as fine small needles, m.p. 206°, yield 0.12 g. (Found: C, 75.19, H, 5.51. $C_{16}H_{14}O_3$ requires : C, 75.55, H, 5.50%). IR spectrum (nujol) : 870 cm^{-1} (furan ring), 1640 cm^{-1} (γ-pyronyl>C=O) ; UV $\lambda_{Max}^{Chloroform}$: 246 nm (log e 4.74), 278 nm (log e 4.60) ; NMR $CDCl_3$) : δ 1.57 – 2.03 (H, m, C_2-H_2 and C_3-H_2), 2.55 (3H, S, C_5-CH_3), 2.40-2.80 (4H, m , C_1-H_2 and C_4-H_2), 6.82 (1H, d, J=2.2 Hz, C_4'-H), 7.68 (1H, d, J=2.2 Hz, C_5'-H), 8.25 (1H, S, C_8-H).

4-Methylfuro(3',2'-2,3)xanthone(III) :

5-Methyl-1,2,3,4-tetrahydrofuro,(2', 3'-6,7)-xanthone 0.6 g) and palladised charcoal (10%,0.8 g) were taken in diphenyl ether (10 ml) and the mixture was refluxed for 10 hr. It was then filtered hot and the solvent was removed by steam distillation. The remaining residue was extracted with ethyl acetate, concentrated and chromatographed on silica gel. Elution with petroleum ether-benzene (1:9) gave the product, which was crystallised from benzene as small needles m.p. 216°, yield 0.2 g. (Found : C, 76.37 ; H, 3.87. $C_{16}H_{10}O_3$ requires : C, 76.81 ; H, 4.00%). NMR ($CDCl_3$) : δ 2.71 (3H, S, C_4-CH_3), 6.89 (1H, d, J=2Hz, C_4'-H), 7.30-7.68 (3H, m, C_5-H, C_6-H and C_7-H), 7.75 (1H, d, J=2Hz, C_5'-H), 8.32 (1H, d, J=10Hz C_8-H), 8.38 (1H, S, C_1-H).

2-Allyl-3-hydroxy-4-methylxanthone (0.5 g) in ethyl acetate (200 ml) and osmium tetroxide (65 mg) in water (70 ml) were vigorously stirred for 15 minutes. Potassium periodate (2 g) was added in small quantities as in case of Ib). The intermediate 5-acetaldehydo product was treated with PPA (15 ml) for 3 hr. at 120°, to give III (0.13 g). It crystallised from benzene as small needles, m.p. 216° (Found : C, 77.21 ; H, 4.36. $C_{16}H_{10}O_3$ requires : C, 76.81 ; H, 4.00%). The mixed m.p. with previously obtained product was not depressed.

1,2,3,4-Tetrahydrofuro (3',2'-5,6) xanthone(V) :

5-Allyl-6-hydroxy-1,2,3,4-tetrahydroxanthone (0.7 g) in ethyl acetate (180 ml) and osmium tetroxide (50 mg) in water (?0 ml) were vigorously stirred for 20 minutes. Potassium periodate (1.5 g) was added in small quantities (as in case of Ib). The intermediate 5-acetaldehydo product was treated with PPA (15 ml) for 4 hr. at 130° to give V (160 mg). It crystalised from benzene as fine needles, m.p. 205°. (Found : C, 74.85 ; H, 4.82. $C_{15}H_{12}O_3$ requires : C, 75.00 ; H, 5.00%). NMR ($CDCl_3$) : δ 1.60-2.50 (4H, m, C_2-H_2 and C_3-H_2), 2.48-2.82 (4H, m, C_1-H_2 and C_4-H_2), 7.08 (1H, d, J=2.2Hz, C_4'-H), 7.46 (1H, d, J=10 Hz C_7-H), 7.70 (1H, d, J=2.2 Hz, C_5'-H), 8.15 (1H, d, J=10Hz, C_8-H).

Furo (2',3'-3',4) xanthone(VI) :

1,2,3,4-tetrahydrofuro (3',2'-5,6) xanthone (0.25 g) and palladised charcoal (0.5 g) were refluxed in diphenyl ether (10 ml) for 12 hr. The reaction mixture worked up as usual gave IV (0.1 g). It crystallised from ethanol as colourless needles, m.p. 191°). (lit[1]., m.p. 192°). (Found : C, 75.86 ; H, 3.56, $C_{15}H_8O_3$ requires C, 76.28 ; H, 3.39%). NMR ($CDCl_3$) : δ 7.10 (1H, d, J=2Hz, C_4'-H), 7.28-7.68 (4H, m, C_2-H, C_5-H, C_6-H and C_7-H), 7.75 (1H, d, J=2Hz, C_5'-H), 8.19 (1H, d, J=10Hz, C_8-H), 8.28 (1H, d, J=10Hz, C_1-H).

4-Allyl-3-hydroxyxanthone (0.5 g) and osmium tetroxide (40mg) were dissolved in ethyl acetate (200 ml) and water (50 ml). Potassium periodate (1.2 g) was added as usual. The intermediate 4-acetaldehydo product, thus obtained was taken in PPA (12 ml) and heated at 130° for 3 hr. to give furo (2′,3′-3,4) xanthone (VI) (0.12 g). It crystallised from ethanol as colourless needles, m.p. 191°. The mixed m.p. with previously obtained product was not depressed.

Acknowledgement

The authors are thankful to Dr. Sukh Dev, Director, Malti Chem Research Centre, Nandesari, Baroda for NMR spectra and the UGC, New Delhi for the award of a research fellowship to one of them (R.J.P.).

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J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 1014-1016

Synthesis of Some 2-(2′-Thienoyl)Coumaran-3-Ones**

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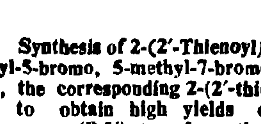
Manuscript received 4 February 1980, revised 30 June 1980, accepted July 26, 1980

Synthesis of 2-(2′-Thienoyl)coumaran-3-one and its 7-methyl, 5-methyl, 5-chloro, 7-methyl-5-bromo, 5-methyl-7-bromo derivatives from two routes have been described. In one, the corresponding 2-(2′-thienoyloxy) acetophenones have been brominated using $CuBr_2$ to obtain high yields of the ω-bromoacetophenones, which on Baker-Venkataraman (B.V) transformation afforded the coumuran-3-ones. In the other, the thienoyloxy acetophenones have been first converted to the related 1:3 diketones by B. V. rearrangement. These ketones have then been converted to the coumaran-3-ones by careful bromination and cyclization.

THE synthesis of 2-acyl coumaranones do not appear to have received much attention[1-11] and in the reports published earlier, the acyl unit was invariably non-heterocyclic. A series of investigations leading to the synthesis of 2-heteroacylcoumaran-3-ones have, therefore, been currently undertaken in this laboratory (partly reported)[12]. In this communication the preparation of some 2-(2′-thienoyl) coumaran-3-ones has been described.

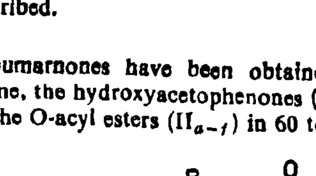
These coumarnones have been obtained by two routes. In one, the hydroxyacetophenones (I_{a-f}) were converted to the O-acyl esters (II_{a-f}) in 60 to 90% yield

I (a-f)

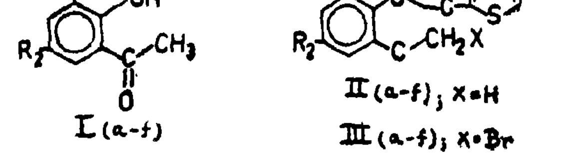


II (a-f); X=H

III (a-f); X=Br



IV (a-f); X=H   V (a-f); X=Br



VI (a-f)   VII (a-f)

a, R_1=H, R_2=H   b, R_1=CH_3, R_2=H
c, R_1=H, R_2=CH_3 d, R_1=H, R_2=Cl
e, R_1=CH_3, R_2=Br   f, R_1=Br, R_2=CH_3

by the direct condensation with thiophene-2-carboxylic acid using $POCl_3$ as the condensing agent[10,13] and the esters were rearranged to the corresponding 1:3-diketones (IV_{a-f}) by Baker-Venkataraman transformation. On careful bromination[5] of the β-diketones (IV_{a-f}) and cyclization of the products the desired coumaranones (VI_{a-f}) were obtained. Repeated crystallisation of the bromo compounds did not yield sharply melting products indicating partial cyclization during purification.

In the second procedure, the intermediate bromo compounds (III_{a-f}) were obtained in high yields by employing dry $CuBr_2$[10,13] for bromination of the esters (II_{a-f}) in conformity with Grover[14] and coworker's observation except, in the case of 3-methyl-2-(2′-thienoyloxy) acetophenone. Baker-Venkataraman rearrangement of these bromo-compounds with KOH in boiling dioxan afforded, (obviously through the unstable intermediate V_{a-f}), the coumaranones identical with those obtained by the first procedure. The overall yields by the second procedure were slightly better than the first. All the coumaranones were soluble in dilute alkali and gave positive ferric reaction. The coumaranones gave the correct elemental analysis results. Their i.r. spectra agree with the assigned structure[15,16] and show distinct hydroxyl bands indicating enolisation to a degree. The PMR spectra of two representative coumaranones add further confirmation.

Experimental

All m.ps are uncorrected. Nuclear brominated hydroxyacetophenones were obtained by the method of Buu-Hoi *et al*[17].

Preparation of the thienoyloxyacetophenones (II_{a-f}):

A mixture of I_a-f (0 06 mole) and thiophene-2-carboxylic acid (0.07 mole) in dry pyridine (10 ml) was treated with $POCl_3$ (2 ml) in drops with stirring (2 hrs)

**Presented at the Annual Convention of Chemists, 1979 held at Kurukshetra University.

below 60°. It was left overnight and poured into ice-HCl mixture. The filtered solid was triturated with NaOH solution (2%), washed with water and recrystallised from ethanol. The m.ps and yields were as under :

II_a 110°, 60%; II_b 72-73°, 78% (Lit.[18] 55°); II_c 91°, 75%; II_d 84°, 65%; II_e 89°, 90%; II_f 82°, 80%.

(In several earlier lots II_b was obtained as a viscous product. The solid analysed correctly for C & H).

Preparation of the 1:3 Diketones (IV_{a-f}) :

II (0.01 mole) and powdered KOH (0.03 mole) in dry pyridine (15 ml) were stirred at 50° till the mixture turned into a thick yellow paste and left at room temperature for 2 hrs. Pouring into crushed ice containing HCl acid gave the crude diketone which was washed and recrystallised from ethanol. The m.ps and yields were as follows :

IV_a 86-87°, 65%; IV_b 79-80°, 80% (Lit.[18] 72-73°, 52%); IV_c 80-81°, 78% (Lit.[18] 80°, 50%); IV_d 106-07°, 60%; IV_e 106°, 75%; IV_f 99-100°, 80%.

Preparation of Coumaran-3-ones (VI_{a-f}) :

A diketone (0.001 mole) in dry chloroform (15 ml) containing anhydrous K_2CO_3 (1g) was treated with bromine (molar proportion) in dry chloroform (5 ml) at 0°. Stirring was continued till the disappearance of the colour due to bromine. The mixture was next refluxed on a water bath (3 hrs) and acidified (dil.HCl). Removal of the chloroform layer, washing, drying ($MgSO_4$) and distillation of the chloroform gave a solid which was crystallised from a proper solvent. The m.ps, yields, solvent of crystallisation have been given in the table separately.

Preparation of ω-Bromo-thienoyloxyacetophenones (III_{a-f}) :

Anhydrous $CuBr_2$ (0.01 mole) in dry dioxan (20 ml) was refluxed for ½ hr. with exclusion of moisture. An ester (II_{a-f}) (0.005 mole) was next added and refluxing was continued for 2 hrs. The dioxan filtrate was concentrated under pump and diluted with ice-water. The solid which separated was washed and crystallised from alcohol. Viscous products were extracted with benzene, purified and directly used for the next experiment. M.ps and yields were : III_a 93°, 82%; III_b gummy mass; III_c 81°, 60%; III_d 90°, 61%; III_e 132°, 60%; III_f 97°, 62%.

Preparation of coumaran-3-ones (VI_{a-f}) :

A ω-bromo ester (0.005 mole) in dry dioxan (15 ml) and powdered KOH (0.015 mole) was refluxed for ½ hr. After cooling, the mixture was poured over ice/dil. H_2SO_4 and the resulting solid was filtered, washed with water and recrystallised.

These products showed no depression on admixture (1:1) with coumaran-3-ones obtained by the other route. The yields have been shown in the table.

TABLE

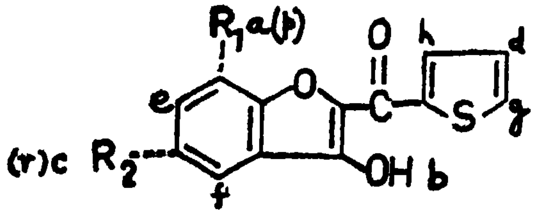
S.N.	Name	M.P.	% yield and solvent of crystallisation.	Mole formula	Required C %	Required H%	Found C%	Found H%
VI_a	(2-(2'-Thienoyl) coumaran-3-one	108-09°	(i) 50 (ii) 80 Ethanol	$C_{13}H_8O_3S$	63.9	3.3	63.4	3.9
VI_b	7-Methyl-2-(2'-thienoyl) coumaran-3-one	145-46°	(i) 45 (ii) 70 Ethanol	$C_{14}H_{10}O_3S$	65.1	3.9	65.0	4.0
VI_c	5-Methyl-2-(2'-thienoyl) coumaran-3-one	140-41°	(i) 65 (ii) 70 Ethanol	$C_{14}H_{10}O_3S$	65.1	3.9	65.2	4.0
VI_d	5-Chloro-2-(2'-thienoyl) coumaran-3-one	153-54°	(i) 60 (ii) 65 Ethanol	$C_{13}H_7O_3ClS$	56.01	2.5	55.9	2.3
VI_e	7-Methyl-5-bromo-2-(2'-thienoyl) coumaran-3-one	174-75°	(i) 70 (ii) 60 Acetic acid	$C_{14}H_9O_3BrS$	49.95	2.67	50.1	2.4
VI_f	5-Methyl-7-bromo-2-(2'-thienoyl) coumaran-3-one	193-94°	(i) 70 (ii) 75 Acetic acid	$C_{14}H_9O_3BrS$	49.95	2.67	50.2	2.7

((i) indicates yield by the first procedure & (ii) by the second)

i.r. data (peaks at cm^{-1}*)*:

VIb, 3150, 1600, 1550 1510, 1300, 1280, 724. VIc, 3150, 1600, 1548, 1516. 1280, 728. VId, 3440, 3100, 1600, 1550, 1505, 1315, 1295, 735. VIe, 3220, 3180, 1600, 1550, 1510, 1320, 730. VIf, 3220, 1590, 1540, 1510, 1320, 720.

PMR data



VIb $R_1 = CH_3$ (Proton labelled 'a')
$R_2 = H$ (,, ,, 'c')
VIc $R_1 = H$ (,, ,, 'p')
$R_2 = CH_3$ (,, ,, 'r')

The PMR spectra of VIb and VIc show the proton resonances (in δ) as follows:

VIb a=2.59, b=6.80, c=7.15, d=7.20, e=7.31, f=7.59, g=7.73, h=8.33.

VIc r=2.49, b=6.00, d=7.23, e=ca 7.36, f=7.53, g=7.73, h=8.38, p=ca 7.36.

In VI_b, the enolic proton 'b' appears as a broad hump centering at 6.80 δ. The methyl protons (3H) show as a singlet at 2.59 δ while the six aromatic protons can be seen as multiplets in the region 7.15-8.33 δ. The proton 'h' comes at a low field centering at 8.33 δ under the influence of the *ortho* carbonyl group and is split into a slightly distorted doublets (J=6Hz). The proton 'c' signals at 7.15 δ as a doublet (J=6Hz).

The exact position of the peaks have been assigned by decoupling experiments (M/S Sadtler Research Laboratories).

Acknowledgement

The authors wish to express their thanks to Prof. J. N. Chatterjea (Patna University) and S. M. Osman (Aligarh Muslim University) for co-operation. M/S Sadtler Research Laboratories Inc., Philadelphia (U.S.A.), have very kindly recorded the PMR spectra and assigned the protons (scanned on Varian CFT-20). They have also recorded the I R. spectra of a few samples (scanned on Digilab FTS 14) and the authors deeply appreciate the help. One of the authors (K R.) gratefully acknowledges the grant of a Teacher Fellowship to him by the U.G.C., and to the authorities of the Bhagalpur University for providing facilities.

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Vol. LVII, October 1980, pp. 1017-1019

Synthesis and Fungitoxicity of Halogenonitrophenyl Esters of N-(propyl, dipropyl, cyclopentyl and dicyclohexyl) Dithioformic Acids

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Manuscript received 6 September 1979, revised 12 May 1980, accepted 26 July 1980

A few halogenonitrophenyl esters of N-(propyl, dipropyl, cyclopentyl and dicyclohexyl), dithioformic acids have been prepared and screened for their antifungal activity against *Alternaria tenuis*, *Helminthosporium sativum* and *Pyricularia oryzae*. They were found to possess significant antifungal activity.

A large number of dithiocarbamates[1] have been known to be potent fungicides. Recently Sen Gupta *et al* have reported the synthesis and insecticidal activity of several new dithiocarbamates[2]. The ability of some halogenonitrophenyl and napthyl esters of piperidino and morpholino-dithiocarbamic acids[3] to exhibit fungicidal activity prompted us to synthesise the title compounds. These were also screened for their antifungal activity.

Experimental

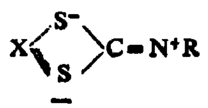
Sodium salt of N-substituted Dithioformic Acid :

A solution of amine ($0.01M$) in methanol (25 ml) was added with stirring to an ice cold solution of sodium hydroxide ($0.01M$) in water (10 ml) with vigorous shaking and maintaining the temperature be ow .°. The mixture was then stirred for another one hour below 10°. The product was filtered and crystallised from methanol to give colourless crystals.

Halogenonitrophenyl Esters of N-substituted Dithioformic Acid :

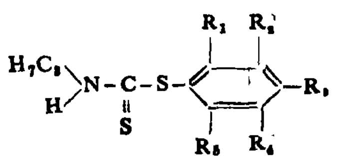
A solution of halogenonitrobenzene ($0.01M$) in ethanol was added dropwise with stirring to a 10% solution of sodium salt of N-substituted dithioformic acid in ethyl alcohol keeping the temperature below 5°. The reaction mixture was stirred until the product separated. The ester was filtered, washed with water and crystallised from alcohol. The structure of these compounds was supported by infrared spectra.

The infra-red spectra of some of these compounds have been recorded in solid state by KBr technique. The I.R. spectra of these esters show a sharp band, around 1642-1480 cm^{-1} characteristic of C=N, partial double bond. The C=N stretching in these compounds shortend under the influence of conical form such as :—



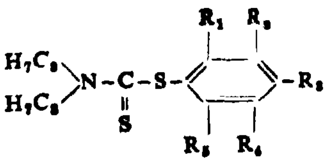
due to the influence of second sulphur atom. The stretching frequencies of C=C in benzene derivatives indicated in the range 1520-1480 cm^{-1} and 1650-1550 cm^{-1} respectively, indicate the presence of a benzene nucleus. Their melting points and analytical data are recorded in Tables 1 to 4.

TABLE 1—ESTER OF N-PROPYL DITHIOFORMIC ACIDS



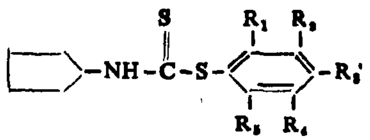
Sr. No.	R_1	R_2	R_3	R_4	R_5	M.P. °C	Ed50 ppm AT	HS	PO
1.	NO_2	H	NO_2	H	H	1200	37	33	39
2.	NO_2	H	H	H	NO_2	155	37	30	37
3.	NO_2	H	NO_2	H	NO_2	65	25	37	30
4.	Cl	H	NO_2	H	NO_2	80	45	50	55
5.	H	Cl	NO_2	H	NO_2	98	72	64	62
6.	NO_2	H	Cl	H	NO_2	100	50	60	50
7.	H	CH_3	NO_2	H	NO_2	87	210	200	164
8.	NO_2	H	CH_3	H	NO_2	113	200	180	210
9.	Cl	Cl	NO_2	H	NO_2	145	64	63	200
10.	Cl	H	NO_2	CH_3	NO_2	168	164	210	180
11.	CH_3	Cl	NO_2	H	NO_2	112	200	250	210
12.	NO_2	CH_3	Cl	H	NO_2	103	150	160	135

TABLE 2—ESTERS OF N-DIPROPYL DITHIOFORMIC ACIDS



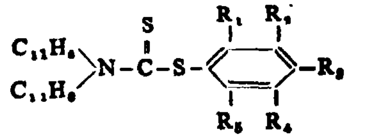
Sr. No.	R_1	R_2	R_3	R_4	R_5	M.P. °C	Ed50 ppm AT	HS	PO
1.	NO_2	H	NO_2	H	H	90	35	33	33
2.	NO_2	H	H	H	NO_2	100	33	30	35
3.	NO_2	H	NO_2	H	NO_2	74	30	32	30
4.	Cl	H	NO_2	H	NO_2	115	35	37	37
5.	H	Cl	NO_2	H	NO_2	125	62	65	60
6.	NO_2	H	Cl	H	NO_2	92	45	47	42
7.	H	CH_3	NO_2	H	NO_2	80	160	165	158
8.	NO_2	H	CH_3	H	NO_2	110	175	200	160
9.	NO_2	CH_3	NO_2	H	NO_2	147	66	60	62
10.	Cl	Cl	NO_2	H	NO_2	150	210	200	180
11.	Cl	H	NO_2	CH_3	NO_2	127	180	165	167
12.	CH_3	Cl	NO_2	H	NO_2	109	150	160	135

TABLE 3—ESTERS OF N-CYCLOPHENYL DITHIOFORMIC ACIDS



Sr. No.	R_1	R_2	R_3	R_4	R_5	M.P. °C	Ed50 ppm AT	HS	PO
1.	NO_2	H	NO_2	H	H	201	50	52	55
2.	NO_2	H	H	H	NO_2	114	45	50	50
3.	NO_2	H	NO_2	H	NO_2	130	40	42	50
4.	Cl	H	NO_2	H	NO_2	125	50	55	60
5.	H	Cl	NO_2	H	NO_2	150	80	75	90
6.	NO_2	H	Cl	H	NO_2	128	68	65	70
7.	H	CH_3	NO_2	H	NO_2	95	100	120	98
8.	NO_2	H	CH_3	H	NO_2	118	90	80	102
9.	Cl	Cl	NO_2	H	NO_2	102	78	68	70
10.	Cl	H	NO_2	CH_3	NO_2	175	200	210	180
11.	CH_3	Cl	NO_2	CH_3	NO_2	115	41	300	250
12.	NO_2	CH_3	Cl	H	NO_2	110	210	200	200

TABLE 4—ESTERS OF DICYCLOHEXYL-DITHIOFORMIC ACIDS



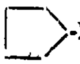
Sr. No.	R_1	R_2	R_3	R_4	R_5	M.P. °C	Ed50 ppm AT	HS	PO
1.	NO_2	H	NO_2	H	H	72	54	46	54
2.	NO_2	H	H	H	NO_2	101	52	50	45
3.	NO_2	H	NO_2	H	NO_2	66	35	50	38
4.	Cl	H	NO_2	H	NO_2	130	53	55	65
5.	H	Cl	NO_2	H	NO_2	176	100	90	98
6.	NO_2	H	Cl	H	NO_2	96	50	52	45
7.	H	CH_3	NO_2	H	NO_2	95	200	250	220
8.	NO_2	H	CH_3	H	NO_2	105	200	90	98
9.	Cl	Cl	NO_2	H	NO_2	99	90	100	150
10.	Cl	H	NO_2	CH_3	NO_2	121	280	300	450
11.	CH_3	Cl	NO_2	H	NO_2	119	400	500	410
12.	NO_2	CH_3	Cl	H	NO_2	165	250	200	220

Screening Results: These compounds were tested for their antifungal activity against *Alternaria tenuis*, *Helminthosporium sativum* and *Pyricularia oryzae* by spore germination method[4]. The dosages in ppm required for the inhibition of 50% growth of fungi have been recorded (Tables 1 to 4).

The fungitoxicity of the esters of N-substituted dithioformic acids depends upon both the ester and the dithioformate moiety. In the ester moiety the fungitoxicity increases sharply when halogen atom or nitro group are placed at ortho or para position in the phenyl ring. However, a halogen atom at meta position seems to decrease fungitoxicity. The effect of methyl group is rather abnormal, when present at ortho or meta position in the phenyl ring of the ester moiety it decreases fungitoxicity. However, when present at the para position the fungitoxicity increases.

In the dithioformate moiety, the presence of lower alkyl groups increases the toxicity. As the number of carbon atom increases the activity decreases. In these compounds, fungitoxicity falls rapidly in the following

order :

$$\begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix} \!\!> N- > C_3H_7NH- >$$  $$>NH- > \begin{matrix} C_6H_{11} \\ C_6H_{11} \end{matrix} \!\!> N-$$

Acknowledgement

The authors are thankful to CSIR, Delhi for the award of a junior fellowship to one of them (P.D.). Thanks are also due to R.S. Kapil (CDRI, Lucknow) for I.R. spectra and C, H. analysis.

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Notes

Stepwise Stability Constants of Indium(III) Complexes with Salicylic and Anthranilic Acid : A Polarographic Study

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Manuscript received 29 April 1979, revised 4 February 1980, accepted 31 March 1980

THE complexing tendency of Salicylic acid and Anthranilic acid with various transition metal ions is well known[1]. Sarin and Munshi[2,3] have reported the stepwise formation constants for Indium(III) complexes with hydroxy and amino substituted analogs of succinic acid and propionic acid, using potentiometric and pH metric techniques.

Polarographic studies[4] of Indium(III) complexes of some amino acids have been reported. n up to date survey of literature reveals that the polarographic studies on the Indium(III) complexes with Salicylic acid and Anthranilic acid have not been made. The present study was undertaken to investigate the composition and stability constants of complexes by making a Deford-Hume[6] treatment of the observed polarographic data.

Experimental

Indium nitrate (Schuchardt Munchen Germany) solution was prepared in 0.2 M perchloric acid medium and was standardised using PAN indicator[5].

The ligand solutions were prepared in 75% v/v aqueous ethanol media. by using Salicylic acid and Anthranilic acid of B.D.H. grade.

The pH of the test solutions was kept constant at 5.0 using potassium hydrogen phthalate buffer and the ionic strength was maintained at 0 2 by the addition of appropriate amount of sodium perchlorate.

An automatic pen recording C I C. (Baroda, India) polarograph was used to record the polarograms. A Philips pH meter was used to measure the pH of the test solutions. Pure hydrogen was passed through the solutions before recording the polarograms. All the measurements were made at the room temperature $27\pm1°$.

Results and Discussion

Indium(III) gives a well defined reversible, three electron reduction wave in 0.2 M sodium perchlorate supporting electrolyte in presence of $2.5\times10^{-5} M$ potassium hydrogen phthalate at pH 5.0. The nature of the wave is diffusion controlled. A similar behaviour was observed for Indium(III) in complex forms. The value of half-wave potential for Indium(III) at this pH is -0.58 volts vs SCE.

On gradual increase of ligand concentration the half-wave potential shifted to more negative value in both the cases (Indium(III) salicylate and Indium(III) anthranilate systems). A Deford-Hume[6] treatment of the data reveals the formation of 1:1 Indium(III) salicylate complex and 1:1 and 1:2 Indium(III) anthranilate complexes. The values of stability constants are given below :

Complex	M:L	Stability Constants
In(III) Salicylate	1:1	$\log \beta_1 = 2.5$
In(III) Anthranilate	1:1	$\log \beta_1 = 5.0$
In(III) Anthranilate	1:2	$\log \beta_2 = 4\ 5$

This difference in stability constants of the complexes of salicylic acid and anthranilic acid may be explained on the basis of the mesomeric effect in anthranilic acid which causes a decrease in proton affinity of NH_2 group which is responsible for the increase of metal ligand stability constants.

Acknowledgement

The author is thankful to the Head, Department of Chemistry, University of Saugar, Sagar, for providing necessary laboratory facilities.

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Stability Constants and Thermodynamic Parameters of Trivalent Gadolinium, Yttrium, Terbium, Dysprosium and Holmium Complexes with 2-(*p*-sulphophenylazo) 1, 8-dihydroxy-naphthalene 3, 6 disulphonic Acid (Trisodium salt) [Spadns]

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Manuscript received 26 March 1979, revised 4 February 1980, accepted 31 March 1980

IN continuation with the work reported[1] from these laboratories on the complexation reactions of SPADNS with La(III), Ce(III), Pr(III), Nd(III) and Sm(III), the work has been further extended with other lanthanides. The stepwise stability constant of Gd(III), Y(III), Tb(III), Dy(III) and Ho(III) complexes with SPADNS have been determined potentiometrically in aqueous solution using Bjerrum-Calvin technique as modified by Irving and Rossotti at different temperatures (20° and 40°) and 0.1 *M* ionic strength ($NaClO_4$). The trend in the stability of these metal complexes has been found to be :

Ho(III) > Dy(III) > Tb(III) > Y(III) > Gd(III)

The overall changes in $\triangle G°$, $\triangle H°$ and $\triangle S°$ accompanying the complex formation have also been determined.

Experimental

Solutions of metal nitrates Gd(III), Tb(III), Dy(III) and Ho(III), (BDH, Anala R Grade) were prepared by dissolving the requisite quantities in conductivity water. The solution of yttrium perchlorate was prepared from Y_2O_3 by the method as reported earlier[1]. All the solutions were standardized by oxalate method[2]. The experimental procedures were the same as reported earlier[1]. *p*H measurements recorded with a Philips *p*H meter (PR 9405*M*) with glass and calomel electrodes at 20° and 40° (maintained in a thermostat). The instrument was calibrated using buffer tablets of *p*H 4 and 7.

Results and Discussion

The proton-ligand stability constants of SPADNS and stepwise stability constants of its complexes with lanthanides were determined using Calvin-Bjerrum[3,4] technique as modified by Irving and Rossotti[5]. The values of proton-ligand stability constants were found to be in close agreement with the values reported earlier[1].

The metal-ligand formation constant values were determined using the following techniques :

(i) Interpolation at half $\bar{n}$ values[3,4], (ii) Least square treatment[6,7] (Curve-fitting method) and (iii) Pointwise calculations method. The final values of log K_1 are given in Table 1.

The values of overall changes in free energy ($\triangle G°$) enthalpy ($\triangle H°$) and entropy ($\triangle S°$) accompanying complex formation have been determined using the standard equations[8]. The values of thermodynamic parameters are also given in Table 1.

From a comparative account of the stability constants it is evident that values are slightly higher at 20° as compared to 40°, indicating that low temperature is favourable for complex formation. The trend in the stability of metal complexes is Ho(III)>Dy(III)>Tb(III)>Y(III)>Gd(III) at 20° and 40°, which is in agreement with accepted view that the stability of lanthanide complexes increases with their decrease in ionic radii.

Lanthanides-SPADNS complex formation is a spontaneous process which is evident from the more negative values of $\triangle G°$ with increase in temperature. The negative values of $\triangle H°$ ensures that the reaction is exothermic. The positive values of $\triangle S°$ indicate that entropy factor is favourable for the complex formation.

TABLE 1 —METAL-LIGAND STABILITY CONSTANTS OF THE COMPLEXES AND THERMODYNAMIC PARAMETERS

Metal ion used	log K_1		$\triangle G°$ (K.Cal.mol^{-1})		$-\triangle H°$ (K.Cal.mol^{-1})	$\triangle S°$ (Cal/mol/C)
	20°C	40°C	20°C	40°C		
Gd^{+3}	8.73	8.46	12.15	11.85	7.84	15.87
Y^{+3}	8.91	8.64	12.35	12.05	8.67	17.90
Tb^{+3}	9.06	8.87	12.85	12.45	10.02	18.15
Dy^{+3}	9.17	8.95	13.05	12.85	11.11	18.85
Ho^{+3}	9.32	9.12	13.25	12.97	11.67	19.10

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Acknowledgement

Thanks of the authors are due to University Grants Commission, New Delhi, for providing a Junior Research Fellowship to one of them (S.N.) and also to Prof. H.L. Bhatnagar, Head of the Chemistry Department for providing laboratory facilities.

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Studies on Se(IV) and Te(IV) Dithiocarbamates

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Manuscript received 30 May 1979, revised 8 January 1980, accepted 31 March 1980

A perusal of literature shows that scarcely attempts have been made earlier for the study of the aforesaid metal dithiocarbamates[1-8]. In continuation of our work on Tellurium(IV)[4] here we report infra-red and thermogravimetric measurements of Se(IV) and Te(IV) complexes of morpholine, piperidine and pyrrolidine dithiocarbamates.

Experimental

Potassium salts of the dithiocarbamates were prepared according to the procedure reported in the literature[5]. The solution of selenium dioxide and potassium tellurite was prepared in distilled water.

Preparation of the Complexes (General Method) :

To a solution of metal(IV) ions (0.1*M*) in water (20 ml.) was added with stirring the solution (0.1*M*) of the potassium salt of the reagent in water (100 ml.). The precipitate was digested on steam-bath for 10 minutes. The complex was filtered, washed with water, finally with ether and dried at 110°–120°.

Results and Discussion

The tellurium(IV) complexes start to lose weight (moisture) at around 90° and completed at 100°. The anhydrous dithiocarbamates decompose sharply at temperature ranging 160–260° [$Te(mdtc)_4$], 158–250° [$Te(pipdtc)_4$], and 126–290° [$Te(pydtc)_4$]. The organic matter completely oxidised at the highest temperature of the aforesaid ranges thereafter a stable region ranging 260–340°, 250–400°, and 290–360°, respectively. In these ranges the formation of tellurium sulphide is concluded which finally oxidised to tellurium oxide. The % of loss in weight observed for different products formed during the heating almost coincide with the % of loss in weight calculated. The DTA confirm the results obtained from TGA

$$Te(dtc)_4 \xrightarrow{\Delta} TeS_2 \xrightarrow{\Delta} TeO_2$$

The selenium complexes become anhydrous after loosing their moisture around '0°. The decomposition of selenium dithiocarbamates of morpholine, piperidine and pyrrolidine start at 150°, 150° and 130° and completed at 280°, 260° and 300° respectively, thereafter a stable region upto 300°, 320° and 400° which is due to the formation of selenium sulphide. The final product of oxidation is selenium oxide. The DTA supports the observation of TGA.

$$Se(dtc)_4 \xrightarrow{-2dtc} Se(dtc)_2 \xrightarrow{\Delta} SeS_2 \xrightarrow{\Delta} Se_2O_2$$

Results of the TGA curves of the complexes (heating rate 5° min^{-1}) indicate that the complexes of morpholine and piperidine dithiocarbamates with the aforesaid ions are thermally more stable than the pyrrolidine dithiocarbamates. The temperatures at which the complex starts decomposition are lower in case of Se(IV) complexes than the Te(IV) complexes. The rigid morpholine ring to release the electron might be a cause of higher decomposition temperature than the piperidine and pyrrolidine dithiocarbamates complexes.

The assignment for the C$\overset{\cdot\cdot}{—}$N and C$\overset{\cdot\cdot}{—}$S stretching frequencies for the complexes are listed in Table-1. The bands in the region 1000–990 cm^{-1} for the latter and 1480–1470 cm^{-1} for the former. The C$\overset{\cdot\cdot}{—}$N mode for diethyl-dithiocarbamate is at 1477 cm^{-1} compared to 1438 cm^{-1} – 1445 cm^{-1} for aforesaid dithiocarbamates This suggest that there is less double bond character in carbon-nitrogen bond. In all the complexes the ligand shows a bidentate nature. It has been reported earlier that complexes having bidentate R_2NCS_2 group exhibit a single ν(C-N) and a ν(C–S)

Table 1

S.No.	Compound	Colour	Elemental analysis Found (Calc.) C%	H%	N%	I.R. Spectra $C\cdots N$ cm^{-1}	$C\cdots S$ cm^{-1}	*p*H for quantitative precipitation
1.	$(MDTC).K$	White	29.31 (29.82)	3.80 (4.00)	6.95 (6.95)	1442	990	—
2.	$(pipDTC).K$	White	35.92 (36.14)	4.91 (5.05)	6.89 (7.02)	1445	990	—
3.	$(pyDTC).K$	White	32.39 (32.39)	4.30 (4.35)	7.48 (7.55)	1438	987	—
4.	$(MDTC)_4Te$	Yellow	30.95 (30.93)	4.13 (4.15)	7.08 (7.21)	1480	1000	3.5–6.5
5.	$(pipDTC)_4Te$	Yellow	37.30 (37.49)	5.19 (5.24)	7.05 (7.28)	1480	1000	3.5–6.0
6.	$(pyDTC)_4Te$	Redish Yellow	33.40 (33.79)	4.27 (4.52)	7.73 (7.86)	1470	995	3.5–6.0
7.	$(MDTC)_4Se$	Light Yellow	32.88 (33.00)	4.17 (4.43)	7.57 (7.69)	1480	980	3.0–5.0
8.	$(pipDTC)_4Se$	Yellow	40.0 (40.03)	5.67 (5.59)	7.48 (7.78)	1480	1000	3.0–5.0
9.	$(pyDTC)_4Se$	Yellow	36.99 (36.17)	4.52 (4.85)	8.51 (8.43)	1475	1000	3.0–5.0

absorptions[6], whereas those containing monodentates $R_2NC(S)S$ group show doublets for the two modes of vibrations[7].

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Studies on the Complexes of Cu(II), Hg(II) and Pb(II) with Benzamidothiosemicarbazide

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Manuscript received 24 August 1978, revised 30 November 1979, accepted 31 March 1980

THIOSEMICARBAZIDE ($NH_2CS\ NH\ NH_2$) and its N-amino derivative (NH_2-NH-CS NH NH_2) thiocarbohydrazide, have long been known to possess biochemical and pharmacological[1] including anticarcenogenic[2], antibacterial and fungicidal[3] properties. They have also been used in the industry[4]. Campbell and Grzeskowiak[5] prepared two series of Cu(II) complexes of thiosemicarbazide and elucidated their structure employing ultraviolet and visible spectroscopic techniques. Ajayi *et al*[6]. reported interaction of Pb(II) with $NH_2C(X)NH\ NH_2$ (X = O, S, Se) and calculated stability constant by polaro graphic method. Stability constant and heat of formation of Hg(II) complex of thiosemicarbazide were determined by Goddard and co-workers[7].

In the present communication the results of our studies on the composition and structural characteristics of benzamidothiosemicarbazide (abbreviated as BTSC) and Cu(II), Hg(II) and Pb(II) have been reported.

Experimental

Benzamidothiosemicarbazide (BTSC) was prepared by the method described by Verma[8] and its solution prepared by dissolving weighed amounts in 80 : 20 ethyl alcohol : water mixture. Fresh solution of BTSC was always used. Stock solutions of copper acetate, mercuric chloride, and lead acetate were prepared by dissolving these salts (B. D. H. 'AR' grade) in doubly distilled air free water. The strengths of these solutions were determined by the usual methods.

Conductometric titrations of BTSC against Cu(II), Hg(II) and Pb(II) were carried out to determine the complexes. A series of solutions keeping the concentration constant and varying the metal (direct titration) and vice-versa (reverse titration) were prepared keeping the volume constant in each case. The plots of conduc-

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tance versus concentration of metal (or ligand) give inflections corresponding to the metal-ligand interaction ratio. Phillips conductivity bridge with dip type conductivity cell (cell constant 0.62) was used for determining the conductance.

Amperometric titrations were carried on a manual polarograph in conjunction with a pye scalamp galvanometer. Both direct and reverse titrations were carried out using $2.0 \times 10^{-2} M$ solution of the metal and the ligand in presence of 0.2*M* KCl as supporting electrolyte and 0.008% gelatine as maximum suppressor. Purified nitrogen was bubbled through the solution for about five minutes after each addition of the titrant for deaeration of the solution. The titrations were carried out at -0.1 volts versus S.C.E. The observed diffusion current was corrected for change in volume during titration by multiplying with $(V+v)/(V)$ and poltted against the volume of the ligand or metal. The inflection points give the interaction ratio of the metal and ligand.

The isolation of these complexes was carried out as given below :—

250 ml of $2.0 \times 10^{-2} M$ aqueous metal salt solution of Cu(II), Hg(II) and Pb(II) was mixed with 500 ml of equimolecular solution of BTSC. The complexes which were white in colour precipitated, cooled and filtered, washed with water and recrystallised with hot methanol and finally dried in a vacuum desiccator. The isolated complexes were analysed for metal and sulphur. The results are given in Table 1.

TABLE 1

Analytical Results

Complex	% of metal Found	% of metal Requires	% of sulphur. Found	% of sulphur. Requires
$(BTSC)_2Cu$	13.2033	13.1879	13.2994	13.2918
$(BTSC)_2Hg$	32.4218	32.4269	10.3460	10.3494
$(BTSC)_2Pb$	33.1034	33.0120	10.2731	10.2400

BTSC = $C_8H_9N_4S$

The magnetic susceptibility measurements were carried out with the help of Gouy's magnetic balance, having a semimicrometer balance, model C Meltlov Zoric type H_{16} No. 140050 at 31°. The observed molar susceptibilities were corrected for diamagnetic contributions.[8] The Cu(II) complex showed a magnetic moment of 1.96 B.M. (corrected molar susceptibility $X_M \times 10^{-6} = 1570$ c.g.s. units).

The i.r. spectra of Cu(II), Hg(II) and Pb(II) complexes of BTSC were taken in KBr medium by the method of fast scanning using 'Beckman I.R. 20'.

Results and Discussion

Preliminary studies show that aqueous solutions of cupric acetate when mixed with a solution of BTSC (prepared in 80 : 20 ethyl alcohol-water mixture) gave a blue black coloured solution which on standing yielded a whitish grey precipitate. In the case of mercuric chloride and lead acetate, rapid precipitation of a white crystalline complex was observed. Investigations on Cu(I) and Hg(I) with BTSC show no interactions. These complexes were characterised by different physico-chemical techniques.

In all the cases sharp breaks were observed for both direct and reverse conductometric titrations. For all the three metals (Cu(II), Hg(II), and Pb(II)) breaks corresponding to 1:2 metal-ligand ratio were obtained.

BTSC gave oxidation currents and the plateau was found to exist at -0.1 volts. Therefore, a constant potential of -0.1 volts was applied for all the amperometric titrations. Normal curves were obtained and gave sharp breaks confirming the stoichiometric results of conductometric studies.

Results of chemical analysis (Table 1) further supported the stoichiometric ratios obtained from electrometric studies.

The Cu(II) complex of composition $Cu(BTSC)_2$ exhibited magnetic moment of 1.96 B. M. which suggested square planar stereochemistry involving sp^2d hybridization.

Hg(II) and Pb(II) complexes of BTSC have $3d^{10}$ configuration and were found to be diamagnetic and possibly had tetrahedral stereochemistry.

The infrared absorption band at 3280 cm^{-1} observed in the infrared spectrum of BTSC was due to NH and NH_2 stretching vibrations. In the Cu(II), and Hg(II) complexes, this band was shifted to higher frequencies 3400 cm^{-1} and 3320 cm^{-1} while in Pb(II) complex this band was broadened in the region 3440 – 3480 cm^{-1} suggesting that the NH_2 group of hydrazine was not involved in the complex formation[9].

The absorption bands, occurring at 1318 cm^{-1}, 790 cm^{-1} and 760 cm^{-1} may be assigned to C=S stretching. Similar assignments have been made for thio acetamide and other thio compounds[10,11]. In the metal complexes, these bands showed a shift to lower wave lengths, the lowering being primarily due to the binding of sulphur to the metal[12]. These bands appear at 1298 cm^{-1}, 745 cm^{-1}, 720 cm^{-1}, for the Cu(II) complex, at 1300 cm^{-1}, 775 cm^{-1}, 735 cm^{-1}, for Hg(II) and at 1310 cm^{-1}, 765 cm^{-1}, 735 cm^{-1} for Pb(II).

The absorption band at 1630 cm^{-1} occurring in ligand spectrum was due to the bending vibrations of the amino and the amide groups. The appearance of tha amide band at the same frequency (1630 cm^{-1}) instead of a decrease indicated the non participation

of the amido nitrogen atom. However, disappearance and lowering of NCS bond frequencies occurring at 1180 cm^{-1} and 1140 cm^{-1} to 1110 cm^{-1} in Cu(II), and at 1160 cm^{-1} and 1110 cm^{-1} in the case of Hg(II) and Pb(II) complexes, indicated the participation of nitrogen atom (attached to amido nitrogen) in bond formation.

The new bands appearing at 460 cm^{-1}, 398 cm^{-1} and at 480 cm^{-1} in the spectra of Cu(II), Hg(II) and Pb(II) complexes respectively were attributed to M-N (metal-nitrogen) stretching frequencies. Further two bands appearing at 330 cm^{-1} and 296 cm^{-1} in the spectrum of Hg-complex and at 340 cm^{-1} and 310 cm^{-1} in the spectrum of Pb(II) complex were assignable to Hg-S and Pb-S stretching frequencies respectively. However, in case of Cu(II) complex very weak M-S absorption bands were observed in the spectrum of copper complex and, therefore, its exact assignment became difficult. The following structure was assigned to these complexes

$$C_6H_5-CO{\cdot}NH{-}N\text{———}C{-}NH{-}NH_2$$
$$M/2 \leftarrow S \quad (N{\mid}\ \text{to}\ M/2;\ C{=}S)$$

M=Cu(II), Hg(II) and Pb(II).

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Schiff Bases as Chelating Agents for Nickel (II)

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Manuscript received 7 August 1978, revised 4 March 1980, accepted 26 July 1980

Two types of ligands were prepared and identified as reported earlier[1-3]. Their general structural formulae are as follows :

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Isolation of Nickel (II) complexes :

On mixing ethanolic solutions of nickel chloride hexahydrate (A.R.) and the corresponding ligands in stoichiometric ratio (1:2) different coloured solutions resulted in separate experiments. The reaction mixture was evaporated nearly on water bath ; methanol (10 ml) was added to it and was left at room temperature for slow evaporation. The coloured crystalline compounds separated out ; which were filtered off, washed with ethanol and then dried in a vacuum desiccator over fused calcium chloride.

General Structures of Schiff Bases :

(I)
$$R-\underset{\underset{CH_3}{|}}{C}=N-R' \; ;$$

(II)
$$R-\underset{\underset{O}{\|}}{C}-CH=N-R'$$

where,

R=4-Acenaphthyl,
4-methyl-7-hydroxy-8-acetocoumaryl,
4-methylphenyl.

R′=2-Carboxylicphenyl, 2-hydroxyphenyl.

Physico – Chemical Measurements and Instruments Used :

The electronic diffuse reflectance spectra were taken in a Ziess PMQ II spectrophotometer with a reflectance attachment RA_3. Electronic spectra in specpure solvents were recorded in a Hilger UVISPEK spectrophotometer using 1 cm cell. Magnetic susceptibility, molar conductance and I. R. spectral studies of the compounds have been made as reported earlier[1-3]. Elemental analysis of the compounds was made at C.D.R.I., Lucknow. Acidic complexes in aqueous and DMSO medium show comparable molar conductance values.

Results and Discussions

All the complexes are soluble in DMF, DMSO, NM and benzene. The molar conductance (λ_M) values indicate their electrolytic as well as nonelectrolytic nature[4].

The room temperature magnetic moments of all the complexes (Table 1) fall within the range 2.83 – 3.45 B. M. expected for octahedral spin free Ni (II) complexes[5].

The diffuse reflectance spectra of the present Ni(II) complexes are characterised by three main bands as shown in Table 2 which are in close agreement to those predicted from Ballhausen and Liehr[6] energy level diagram for Ni(II) ions in O_h symmetry. The results are more or less in good agreement with those reported

TABLE 1—ANALYTICAL DATA AND OTHER PROPERTIES OF THE COMPLEXES

Complex	Colour	% El mental analysis N Calcd. (Found)	C Calcd. (Found)	Ni Calcd. (Found)	μ_{eff} in B.M. (303°K)	λ_M Ohm^{-1} mole^{-1} cm^2 DMSO (Aqueous)
$H_2[Ni(C_{21}H_{16}NO_3)_2Cl_2]$	Pale blue	3.68 (3.60)	66.31 (65.80)	7.76 (7.58)	3.06	210 (190)
$[Ni(C_{20}H_{14}NO_2)_2]$	Blue	4.24 (4.14)	72.84 (72.06)	8.95 (8.82)	3.14	28
$H_2[Ni(C_{19}H_{13}NO_5)_2]$	Blue	3.83 (3.75)	62.40 (61.99)	8.33 (8.48)	3.02	175 (160)
$H_2[Ni(C_{18}H_{13}NO_4)_2]$	Green blue	4.15 (4.14)	64.02 (63.54)	8.70 (8.62)	2.98	198 (175)
$[Ni(C_{16}H_{12}NO_3)_2]$	Pale blue	4.74 (4.68)	65.00 (64.38)	9.93 (9.85)	3.11	35
$[Ni(C_{15}H_{12}NO_2)_2]$	Yellow, green	5.20 (5.14)	67.07 (66.82)	10.93 (11.01)	3.17	40

TABLE 2—PRINCIPAL BAND POSITIONS IN THE REFLECTANCE SPECTRA WITH PROBABLE ASSIGNMENTS AND THE LIGAND FIELD PARAMENTERS

Complex	Band positions (cm^{-1}) and their assignments $^3A_{2g}(F)$ ⟶ $^3T_{2g}(F)$ ν_1	$^3T_{1g}(F)$ ν_2	$^3T_{1g}(P)$ ν_3	Splitting energy 10D$_q$ (cm^{-1})	Racah Parameter B (cm^{-1})	B	ν_2 Calcd. (cm^{-1})	ν_3 Calcd. (cm^{-1})	ν_2/ν_1
$H_2[(C_{21}H_{16}NO_3)_2Cl_2]$	9,800	15,610	25,800	9,800	800	0.74	15,760	25,517	1.59
$[Ni(C_{20}H_{14}NO_2)_2]$	10,800	17,000	26,000	10,800	707	0.65	16,700	26,300	1.57
$H_2[Ni(C_{19}H_{13}NO_4)_2]$	10,500	16,600	26,000	10,500	740	0.69	16,415	26,140	1.58
$[Ni(C_{16}H_{12}NO_3)_2]$	10,800	16,800	26,000	10,800	693	0.64	16,700	26,050	1.55
$[Ni(C_{15}H_{12}NO_2)_2]$	10,400	16,900	29,130	10,400	989	0.91	16,020	28,780	1.62
$H_2[Ni(C_{19}H_{18}NO_5)_2]$	10,100	16,800	25,400	10,100	793	0.73	16,120	26,100	1.66

for octahedral Ni(II) complexes[7-8]. Although the diffuse reflectance and solvent spectra of the complexes are similar but the former shows three insignificant extra shoulders at about 6000 cm^{-1}, 7000 cm^{-1} and 13000 cm^{-1}. These can be due to ligand overtones, some lowering in symmetry[9] and spin forbidden transitions $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ as suggested by Jorgensen[10].

I. R. Spectra :

A comparison of i.r. spectra of the ligands with those of Ni(II) complexes indicates lowering of stretching frequency due to azomethine (=C=N–or–CH=N–) group as ~1600 to ~1580 cm^{-1}. This shifting of frequencies suggests the formation of metal nitrogen bond which is further confirmed by the appearance of bands[11] at ~500 cm^{-1}. Anthranilic acido ligands exhibit bands[12] at ~2700 cm^{-1} due to –OH of carboxylic group, however, these bands are shifted in the complexes due to deprotonation.

Phenolato ligands consist of stretching frequency due to ν(OH) at ~3400 cm^{-1}, however, these frequencies are also shifted because of complexation with Ni(II). Thus the formation of metal-oxygen (M–O) bonds[13] occurs which is confirmed by the appearance of bands at ~400 cm^{-1}. The acyl ligands show bands at ~1700 cm^{-1} due to acyl group, however, these stretching frequencies are lowered in the complexes due to chelation through oxygen of ketonic group.

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2-Hydroxy-4-Methylpropiophenone oxime as an Analytical Reagent : Studies on Nickel Complex

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Manuscript received 11 October 1976, revised 14 February 1980, accepted 31 March 1980

THE well known reagents for gravimetric determination of nickel are dimethylglyoxime[1], nioxime[2], resacetophenone oxime[3]. 2-Hydroxy-5-methylpropiophenone oxime[4], 2-hydroxy-4-methylacetophenone oxime[5] and 5-ethylresacetophenone oxime[6] have been used as analytical reagents for nickel. In a project designed to develop new organic reagents for the determination of metal ions the use of 2-hydroxy-4-methylpropiophenone oxime has been investigated as a gravimetric reagent for Ni(II). An ethanolic solution of the reagent reacts with Ni(II) quantitatively forming a green complex of 1:2 stoichiometry analysing for $Ni(C_{10}H_{12}O_2N)_2$. The Ni(II) complex is insoluble in hot water and hot aq. ethanol (60 – 70% v/v). The complex can be dried without decomposition at 110 – 20° and is directly weighable as $Ni(C_{10}H_{12}O_2N)_2$. Cations like aluminium(III), cadmium(II), lead(II), zinc(II), mercury(II), barium(II), calcium(II), manganese(II), cobalt(II), magnesium(II) and anions like tartrate, citrate, chloride, nitrate are found not to interfere at *p*H range 5.0 to 5.5. Interference of Fe(III) was removed by masking with sodium potassium tartrate before adding the reagent. Gravimetric determination of copper and nickel in their binary mixture has been carried out with satisfactory results taking advantage of the different *p*H range for precipitation.

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Experimental

All the chemicals used were of A. R. grade. Stock solutions of metal ions were prepared by dissolving pure salts in double distilled water and were employed after standardisation by standard methods.

Ammonium hydroxide and acetic acid were used to prepare buffers of different *p*H values.

Reagent : 2-Hydroxy-4-methylpropiophenone Oxime :

2-Hydroxy-4-methylpropiophenone[7] was obtained in almost quantitative yield by Fries migration of m-cresyl propionate[8] in presence of anhydrous aluminium chloride. Its oxime[7] was prepared by refluxing its alcoholic solution with hydroxylamine hydrochloride and potassium hydroxide (40%). It was purified by repeated crystallisation from petroleum, m.p. 104°.

Gravimetric estimation of Ni(II) : An aliquot of standard solution of Ni(II) containing 6 to 30 mg of Ni(II) was diluted to 150 ml and *p*H was adjusted to 5.5 using ammonia and acetic acid buffer. The contents were heated to 60 – 70° and treated with 1% ethanolic solution of 2-hydroxy-4-methylpropiophenone oxime added dropwise with constant stirring (about twice the theoretical amount). The green precipitate obtained was digested on a water-bath for 30 min and filtered through a G-4 sintered glass crucible. It was washed with hot water several times and finally with 60% ethanol and dried at 110 – 20° to a constant weight. It has been found that the precipitation of nickel is quantiative in the *p*H range 5.0 – 10.0 The conversion factor (nickel/nickel complex) is 0.1416. Some representative results are given in Table 1.

TABLE 1 – DETERMINATION OF Ni(II)

Ni(II) taken (mg)	Ni(II) found (mg)	Error (%)
5.94	5.92	– 0.34
11.88	11.85	– 0.25
	11.82	– 0.51
14.85	14.87	+ 0.13
	14.85	± 0.00
20.79	20.81	+ 0.096
	20.85	+ 0.29
29.70	29.8	+ 0.34

Precision and accuracy: The relative standard deviation in the determination of nickel (14.85 mg) by the given method was ±0.4% in 20 determinations.

Determination of nickel in the presence of other ions: The procedure was the same as in the absence of foreign ions. The interference in some cases was removed by working at low *p*H to prevent the precipitation of corresponding hydroxides. Interference due to Fe(III) was removed by adding potassium tartrate. By suitable adjustment of *p*H, a number of cations and anions could be tolerated e.g., Ca(II) and Ba(II) (about 20 times), Al(III), Cd(II), Pb(II), Zn(II), Hg(II), Mn(II), Co(II), (about 2 to 3 times), Mg(II) (about 10 times), large amount of tartrate, citrate, chloride and nitrate could be tolerated at *p*H 5.0 to 5.5.

From the solution containing both copper and nickel, copper was first precipitated and estimated at *p*H 3.0 as reported[9] earlier and from the filtrate nickel was precipitated by addition of more reagent and adjustment of *p*H 5.0 to 5.5 as indicated above. The results are reproducible with an error ±0.4% for amounts of Ni(II) ranging from 2.97 to 15.0 mg. The reagent is readily prepared and less expensive.

Composition of the complex: The nickel complex was analysed to determine the composition. (Found: Ni, 13.68; N, 6.62, Calc: Ni, 14.16; N, 6.75%). The molecular weight determined cryoscopically using camphor as solvent showed the complex to be monomeric, i.e., the complex could be represented by ML_2. The 1:2 composition of the complex was confirmed by Job's method of continuous variation, potentiometric and conductometric studies. The formula of the complex may therefore be represented as $Ni(C_{10}H_{12}O_2N)_2$. The complex can be extracted in benzene, chloroform and carbon tetrachloride.

Examination of the IR spectrum of the reagent showed strong bands at 3400 cm^{-1} (ν OH chelated), 2980 cm^{-1} (ν OH of=N–OH), 1640 cm^{-1} (ν C=N), 980 cm^{-1} (ν N–O) and 790 cm^{-1} (1,2,4 trisubstituted benzene). Examination of the IR spectrum of the chelate shows that the phenolic hydrogen is replaced by the metal because the band at 2980 cm^{-1} due to hydroxy group of the oximino moiety appears more or less at the same position in both the ligand and the complex and 3400 cm^{-1} peak of the chelated OH disappears in the complex. In the chelate the band at 1640 cm^{-1} disappears and a stronger band appears at 1610 cm^{-1}, which may be assigned to C=N shifting down field, due to complexation.

The UV and visible spectra were mapped using solution of this complex in chloroform and peaks at 300 nm, 375 nm and 600 nm were obtained. The magnetic susceptibility of this chelate showed that it is diamagnetic in character.

Acknowledgement

The authors are indebted to Principal, Gujarat College, Ahmedabad for providing research facilities. Thanks are due to S. P. University, Vallabh-Vidyanagar for UV and visible spectra and Cadila Laboratories, Ahmedabad for IR spectra.

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Effect of UV Light on Aqueous Solution of Tartaric Acid in the Presence of Nitrogen under Heterogeneous Conditions

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Manuscript received 14 June 1979, accepted 31 March 1980

SYNTHESIS of specific life forming molecules is at present being investigated under conditions believed to have existed in the prebiological era of earth. The problem of abiotic synthesis of such compounds has been discussed by a number of workers i. e., Oparin, Haldane, Miller, Ponnamperuma and others[1-9]. They have emphasised that the molecules that are fundamental today were fundamental at the time of abiogenesis of living matter. It has been suggested that in the ancient abiotic periods of earth, diverse types of organic compounds would have been formed by various methods which would not have required any kind of living or vital forces. Tartaric acid one of such compounds under nitrogen atmosphere was irradiated by ultraviolet light with a view to see the formation of life forming molecules.

It is well known that tartaric acid in aqueous solution decomposes rapidly when exposed to UV light giving a variety of products[10-12]. However, the action of UV light on aqueous solution of tartaric acid under nitrogen atmosphere has not yet been studied. Therefore, it was considered of interest and the effect of UV light on aqueous solutions of tartaric acid in the

presence of sensitizers and nitrogen atmosphere has been studied and the results have been presented in this communication.

Materials and Methods :

Extra pure tartaric acid (0.1%, B. D. H./E. M) solution was prepared in redistilled water and 250 ml of this solution was taken in each of four sterilized quartz glass vessels. Extra pure organic and inorganic sensitizers were then added to these vessels under asceptic conditions. The purity of sensitizers was tested prior to their addition to the experimental solutions. These flasks were connected with each other by stetrilized glass connecting tubes and kept under UV irradiation chamber. The inlet of the gas passing tubes was connected with nitrogen gas generating unit. Nitrogen gas was prepared freshly (by using extra pure $NH_4Cl+NaNO_2$) and passed through dilute H_2SO_4 and water in order to wash out ammonia. The pure gas was then bubbled through the sterilized solutions in quartz flasks kept in UV irradiation chamber. The solutions were first satutared with N_2 for an hour by passing a contineous stream of gas and then exposed to ultraviolet source upto 25 hr. Contineous stream of N_2 was passed through out the course of the experiment. The exposed solutions were drawn out asceptically, concentrated in a rotatory vacuum evaporator, examined for any microbial contamination by usual techniques[13-14] and then the portions of the concentrates were analysed chromatographically employing Whatman No. 1 paper (18.5×22.5", 24 hr at 20±2°), Sillica Gel G or Cellulose layer (MN 300) as stationery phase and n-butanol : acetic acid : water (4 : 1 : 1, v/v ; 9 : 1 : 1, v/v) or butanol : acetic acid : pyridine : water (15 : 3 : 12 : 10, v/v) as solvent systems. The authentic amino acids were run concurrently alongside of the concentrate as reference standards. The chromatogram was first dried in air, then at 60°, examined under UV black light lamp for marking fluorescent spots and eluted with water for further characterization. For locating and charactering the resulting products ninhydrin (0.1 g/100 ml acetone), alloxan (0.2 g/100 ml acetone), isatin (0.2 g/100 ml acetone), and Folin's reagent (0.02% 1-2 naphthaquinone-4-sulphonate in 5% aqueous sodium carbonate) were used as colour producing reagents.

Dinitrophenyl derivatives of provisionally identified amino acids were prepared and characterized by comparing their properties with authentic DNP amino acids as reported in our earlier communications[8-9]. Thus the photolytic products were characterized by their comparison with the authentic DNP amino acids, R_f values, m.p. mixed m.p. of DNP derivatives coincidence chromatography, noting their characteristic fluorescence under UV black light lamp (3650 Å) and also by specific chemical and spectral methods.

Results and Discussion

When an aqueous solution of tartaric acid in the presence of potassium dihydrogen phosphate under N_2 atmosphere was exposed to UV light for 1 hr, appearance of a product II in poor amounts was noticed. When exposure time was incresed to 5 hr, two new products III and IV were detected on the chromatogram. On prolonging the irradiation period upto 25 hr products I, V and VI appeared on the papergram in addition to the products observed for 5 hr exposure to UV light. However, the concentration of all the products increased on increasing the irradiation period upto 25 hr. When sodium molybdate, titanium dioxide, acenaphthene were used as sensitizers in aqueous solutions of tartaric acid under nitrogen atmosphere for the same period of irradiation (25 hr), no new ninhydrin positive compound could be detected except those observed when aqueous solution of tartaric acid was exposed to UV light in the presence of potassium dihydrogen phosphate. Out of these six products formed, four products were tentatively characterized as glycine (II), α-alanine (III), α-amino-n-butyric acid (V) and valine (VI). Results are reported in Table 1.

TABLE 1—RESULTS OF UV IRRADIATION (25 hr) OF TARTARIC ACID IN THE PRESENCE OF N_2 GAS UNDER HETEROGENEUOS CONDITIONS

Reaction Mixture	Products of photochemical synthesis I	II	III	IV	V	VI
Tr W N_2 KP	+	Gly	Ala	+	Buty	Val
Tr W N_2 NaM	+	Gly	Ala	+	Buty	Val
Tr W N_2 TiO_2	+	Gly	Ala	+	Buty	Val
Tr W N_2 Ac	+	Gly	Ala	+	Buty	Val
R_f^{*1}	.06	0.12	0.16	0.22	0.32	0.42
Colour with ninhydrin	VR	RV	V	Y	V	V
Alloxan	R	P	RP	—	RP	R
Isatin	—	BrP	DB	—	VB	RP
Folin's Reagent	—	GP	GB	—	GB	BGr
O-Phthalal dehyde	—	GR	—	—	—	—
DNP. Dvts.						
R_f^{**}	—	0.34	0.48	—	0.49	0.58
m.p.	—	201°C	170°C	—	—	130°C
Fluorescence in UV black light lamp	W	BW	W	W	BV	BV

—, not detected ; +, positive test or poor yield ; W, water or white ; Y, yellow ; B, Blue ; R, red ; V, violet ; G, grayish ; Gr, green ; P, purple, D, dark ; KP, potassium dihydrogen phosphate ; NaM, sodium molybdate ; Ac, acenaphthene ; Tr, tartaric acid ; Gly, glycine ; Ala, alanine ; Buty, α-amino-n-butyric acid ; Val, valine ; *, in n-butanol:acetic acid:water (4:1:1, V/V) at 20-12°C, *, in tert amyl alcohol-3% ammonia (1:1, V/V).

Product III resembled glycine in its resolution factor (0.12), coincidence chromatography, m.p of DNP derivative (201°) and colour reaction with naphthaquinone reagent (greenish purple), ninhydrin (red violet), isatin (brownish purple) and alloxan (purple). The identity of this compound as glycine was further ascertained by the appearance of green colour with o-phthalaldehyde which turned purple on adding urea (.2%) to the reaction mixture and brown on exposure to UV light of 365 m μ. It on ninhydrin mediated oxidative degradation, afforded, like authentic glycine, formaldehyde, which was detected with cromotropic acid. Absorption spectra of both products II and authentic glycine showed λ_{max} 2100.

Product III when deaminated with nitrous acid (10% HCl+5% $NaNO_2$) in micro capillary tube and the liberated product on oxidation with acid permanganate gave acetaldehyde which gave blue colour with Rimini reagent. One ml of this reagent (10% dimethyl aminobenzaldehyde in HCl) was diluted to four volumes of acetone before use. Being acidic in nature it destroyed the colour produced by ninhydrin and a purple yellow colour was appeared exactly similar to that of authentic α-alanine.

Product V was identified as α-amino-n-butyric acid by its R_f value (0.37), co-chromatography and reaction with ninhydrin (violet) alloxan (purple), Folin's reagent (greenish blue) and isatin (violet blue). Its DNP derivative (m.p. 132°) resembled with that of authentic α-amino-n-butyric acid. Product VI was characterized as valine by the identity of its R_f (0.40), co-chromatography and characteristic colours with ninhydrin (violet), isatin (reddish purple), alloxan (red) and Folin's reagent (bluish green) with that of valine. This product showed bluish white fluorescence under UV black light lamp. Other properties of the products are recorded in Table 1.

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Influence of Some Complexing Agents on the Reactivity of Indian Rock Phosphates

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Manuscript received 21 November 1979, revised 22 April 1980, accepted 26 July 1980

FROM a study of the action of some complexing agents on the reactivity of various Indian rock phosphates it appears that the complex forming capacity of the agent with the ingredients of the rock phosphates plays a decisive role in releasing more phosphate in solution. The amount of phosphate passing into the solution increases with the lapse of time to a marked extent which may be due to the hydrolysis and subsequent complex formation. The efficiency of phosphate release by complexing agents used varies in the order of EDTA > Oxine > Cupferron > Dimethyl glyoxime. A number of contradictory reports have recently appeared in literature regarding the reactivity of Indian rock phosphates[1,2]. According to Vaid[3] almost all the rich reserves of Rajasthan rock phosphates except only 8% of the Jhamar Kotra rock are less reactive and can not be used without concentration. Hajra and Chakravarti[4] advocated the use of some chelating agents for increasing the release of phosphates from insoluble iron and aluminium phosphate minerals. In the present investigation an attempt has therefore been made to study the effect of some complexing agents on the reactivity of various rock phosphates so as to ascertain the economic utility of these phosphates avilable in abundance in different parts of India.

Experimental

Rock phosphates from Rajasthan, Uttar Pradesh and Bihar obtained through Geological Survey of India were powdered, sieved through a 100 mesh sieve (B.S.S.) and analysed in accordance with the procedure described by Washington[5].

TABLE 1—COMPOSITION OF DIFFERENT ROCK PHOSPHATES

Ingredients	RP	MNP	MPS	MGP	MVLP	MRP	I(B)RP
Insoluble material	5.60	7.56	26.05	5.90	17.26	3.24	24.14
Al_2O_3	1.42	23.05	23.92	25.51	33.90	31.26	18.96
Fe_2O_3	0.28	0.25	0.24	0.25	0.32	0.96	12.17
CaO	44.98	32.15	17.00	16.45	15.50	11.38	9.81
MgO	0.08	0.09	0.06	0.05	0.05	0.04	0.35
P_2O_5	27.18	15.46	10.34	30.17	11.97	30.72	15.60

RP = Rajasthan Phosphate, MNP = Mussorie Nodular Phosphorite, MPS = Mussorie Phosphorite Shale, MGP = Mussorie Granular Phasphorite, MVLP = Mussorie Variegated Lenticular Phosphorite, MRP = Mussorie Rock Phosphate, I(B)RP = Itagarh (Bihar) Rock Phosphate.

1 g finely powdered samples of each rock phosphate were treated with 0.1 g EDTA, oxine, cupferron, dimethyl glyoxime and 100 ml distilled water taken in different 250 ml stoppered pyrex conical flasks. After recording the initial *p*H values, each set was neutralized using either 0.1 *N* HCl or 0.1 *N* NaOH so as to bring *p*H value at 7. The systems were treated with a few drops of chloroform in order to check fungus growth. The contents of the flasks were stirred daily. Different sets were used for different intervals of time. After definite interval of time the flasks were shaken for half an hour in a mechanical shaker, allowed to stand for some time and then filtered. Aliquot portions were utilized for determining P_2O_5 and *p*H[6]. P_2O_5 was estimated by the method described by Hajra and Chakravarti[4]. For blank (mineral & water) estimations 1 g powdered samples of each rock phosphate were treated with 100 ml distilled water, few drops of chloroform and kept for 7 days. The results are tabulated.

Results and Discussion

The analysis shows that all the rock phosphates contain appreciable amounts of P_2O_5, calcium, magnesium and iron, suitable for healthy plant growth. It is interesting to note that all the phosphates are alkaline in nature.

It can be reckoned from the Table 2 that the release of P_2O_5 from rock phosphates by water is not much and when complexing agents are used the release increases to a marked extent. On addition of EDTA/Oxine for each system there is a slight lowering of *p*H at the initial stage but on prolonged incubation *p*H values tend to return to the original level. This is due to the liberation of H^+ ions in the medium as a result of the instantaneous interaction between the metal ions of the rock phosphates and EDTA/Oxine. However, with the lapse of time hydrolysis of the remaining uncombined rock phosphates occur resulting in the rise of *p*H values of the systems. With other complexing agents the *p*H values of the systems increase at the initial stage. This may be due to the fact that there is not much complex formation reactions with these agents and a slight increase in *p*H values at the initial stage occurs on account of hydrolysis of rock phosphates. Further increase in *p*H values in all the systems with the lapse of time is due to the hydrolysis of rock phosphates.

Thus complexing agents help to decompose the rock phosphates in the initial stage and once the decomposition starts it is followed by the hydrolysis of the remaining rock phosphates which continues with the lapse of time releasing more P_2O_5 in the solution. The degree of decomposing influence of the complexing

TABLE 2(a)—BLANK (MINERAL & WATER) ESTIMATION

Phosphates	*p*H Initial	*p*H After 7 days	P_2O_5 (g/g of the phosphate) Initial	P_2O_5 (g/g of the phosphate) After 7 days
RP	7.20	7.60	0.48×10^{-4}	0.50×10^{-4}
MNP	7.15	7.55	0.40 ,,	0.40 ,,
MPS	7.05	7.35	0.10 ,,	0.08 ,,
MGP	7.05	7.30	0.38 ,,	0.32 ,,
MVLP	7.10	7.30	0.08 ,,	0.10 ,,
MRP	7.05	7.25	0.30 ,,	0.30 ,,
I(B)RP	7.10	7.30	0.22 ,,	0.20 ,,

TABLE 2(b) – INFLUENCE OF COMPLEXING AGENTS ON THE REACTIVITY OF VARIOUS ROCK PHOSPHATES

Period	Phosphate	EDTA		Oxine		Cupferron		Dimethyl glyoxime	
		pH	P_2O_5(g/g)	pH	P_2O_5(g/g)	pH	P_2O_5 (g/g)	pH	P_2O_5(g/g)
Initial Stage	RP	6.40	0.60×10^{-2}	6.80	0.58×10^{-2}	7.25	0.54×10^{-2}	7.25	0.52×10^{-2}
	MNP	6.40	0.54 ,,	6.55	0.52 ,,	7.20	0.48 ,,	7.20	0.46 ,,
	MPS	6.45	0.16 ,,	6.45	0.14 ,,	7.10	0.14 ,,	7.10	0.12 ,,
	MGP	6.45	0.42 ,,	6.40	0.40 ,,	7.10	0.38 ,,	7.10	0.36 ,,
	MVLP	6.50	0.16 ,,	6.30	0.48 ,,	7.15	0.12 ,,	7.15	0.10 ,,
	MRP	6.50	0.36 ,,	6.30	0.38 ,,	7.10	0.34 ,,	7.10	0.32 ,,
	I(B)RP	6.60	0.28 ,,	6.40	0.30 ,,	7.15	0.26 ,,	7.15	0.24 ,,
After 24 hours	RP	7.40	0.94×10^{-2}	7.35	0.88×10^{-2}	7.30	0.82×10^{-2}	7.30	0.78×10^{-2}
	MNP	7.35	0.86 ,,	7.30	0.80 ,,	7.25	0.74 ,,	7.25	0.70 ,,
	MPS	7.25	0.28 ,,	7.20	0.22 ,,	7.15	0.20 ,,	7.15	0.18 ,,
	MGP	7.25	0.68 ,,	7.20	0.62 ,,	7.15	0.58 ,,	7.15	0.60 ,,
	MVLP	7.30	0.30 ,,	7.25	0.74 ,,	7.20	0.20 ,,	7.20	0.16 ,,
	MRP	7.25	0.58 ,,	7.20	0.60 ,,	7.15	0.52 ,,	7.15	0.48 ,,
	I(B) RP	7.30	0.46 ,,	7.25	0.48 ,,	7.20	0.40 ,,	7.20	0.36 ,,
After 3 days	RP	7.60	0.30×10^{-2}	7.50	0.27×10^{-2}	7.45	0.24×10^{-2}	7.40	0.22×10^{-2}
	MNP	7.55	0.27 ,,	7.45	0.24 ,,	7.40	0.21 ,,	7.35	0.20 ,,
	MPS	7.45	0.08 ,,	7.35	0.06 ,,	7.30	0.04 ,,	7.25	0.04 ,,
	MGP	7.45	0.20 ,,	7.35	0.18 ,,	7.30	0.18 ,,	7.25	0.16 ,,
	MVLP	7.50	0.08 ,,	7.40	0.22 ,,	7.35	0.06 ,,	7.30	0.06 ,,
	MRP	7.45	0.18 ,,	7.35	0.20 ,,	7.30	0.16 ,,	7.25	0.16 ,,
	I(B)RP	7.50	0.14 ,,	7.35	0.16 ,,	7.30	0.12 ,,	7.25	0.10 ,,
After 7 days	RP	7.85	0.70×10^{-2}	7.80	0.64×10^{-2}	7.75	0.56×10^{-2}	7.70	0.64×10^{-2}
	MNP	7.75	0.60 ,,	7.70	0.56 ,,	7.65	0.48 ,,	7.60	0.46 ,,
	MPS	7.65	0.21 ,,	7.60	0.16 ,,	7.50	0.14 ,,	7.45	0.12 ,,
	MGP	7.60	0.48 ,,	7.55	0.42 ,,	7.45	0.40 ,,	7.40	0.38 ,,
	MVLP	7.65	0.22 ,,	7.60	0.48 ,,	7.55	0.14 ,,	7.50	0.12 ,,
	MRP	7.60	0.42 ,,	7.55	0.44 ,,	7.50	0.36 ,,	7.45	0.34 ,,
	I(B)RP	7.55	0.35 ,,	7.50	0.36 ,,	7.45	0.28 ,,	7.40	0.22 ,,

agents used varies in the order of EDTA>Oxine>Cupferron>Dimethyl glyoxime. This may be due to the fact that the rock phosphates contain more calcium than other ingredients like aluminium, iron and magnesium.

This investigation clearly reveals that the reactivity of Indian rock phosphates increases in presence of complexing agents. As metal chelates are better source of micronutrient supply to plants[7,8,9] rock phosphates with a small quantity of complexing agents are very useful for supplying micronutrient elements and phosphorus to plants.

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Composition of Essential oil of *Elsholtzia strobilifera* Benth

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Manuscript received 22 April 1980, accepted 26 July 1980

ELSHOLTZIA strobilifera Benth (N. O. Labiatae), a medicinal-aromatic species, posseses high content of essential oil. The oil has been found to possess antibacterial and antifungal properties[1,2]. The light yellow coloured essential oil from the fresh plant material was extracted by steam distillation in 0.4% yield. The essential oil was dried over anhydrous sodium sulphate and the physico-chemical properties determined by the conventional methods are : specific gravity = 0.9096/20°, ref. index = 1.4890/20°, sp. rotation = + 4.1, acid value = 0.64, ester value = 13.79, ester value after acetylation = 49.9 and carbonyl value = 49.3.

The essential oil (*100 ml*) was first separated into hydrocarbon and oxygenated fractions by column chromatography[4]. These were then subjected to fractional distillation under reduced pressure (4-5 mm). Each fraction was purified by column chromatography using silica gel BDH (60-120 mesh) as adsorbent. Purity of the fractions was ascertained by TLC over silica gel coated plates in different solvent systems. In all eleven fractions were obtained and out of these *10* compounds were identified by preparing their characteristic derivatives[5]. The presence of β-pinene, α-phellandrene, dipentene, bisabolene, 1, 8-cineole, linalool, terpinen-4-ol, carvone, citronellol and geranyl acetate was established.

The major fraction (38%) gave tests for a keto compound (2,4-DNP, m.p. 146°). The IR spectrum gave strong bands at 3000, 2960 – 2910, 1720 and 1640 cm^{-1}, medium intensity bands at 1480, 1400, 1380, 1346, 1300, and 1070 cm^{-1} and weak bands at 840 and 610 cm^{-1}. The mass spectrum of the compound ($C_{10}H_{16}O$) gave molecular ion peak at m/e = 152, the base peak at 55 and other prominent peaks at 40, 95, 83, 69 and 41. The structure is yet to be established with the help of PMR and C^{13} NMR.

TABLE—GLC OF ESSENTIAL OIL OF *Elsholtzia strobilifera*

Peak No.	Relative retention time (dipentene = 1)	Percentage in the oil	Compound identified
1	0.3	0.55	α-pinene
2	0.4	12.14	β-pinene
3	0.7	0.5	myrcene
4	0.8	1.8	α-phellandrene
5	1.0	10.4	dipentene
6	1.4	5.5	1,8-cineole
7	1.6	trace	γ-terpinene
8	1.8	0.15	*p*-cymene
9	2.5	1.9	linalool
10	3.0	trace	linalyl acetate
11	3.4	trace	bornyl acetate
12	4.2	trace	unidentified
13	4.4	3.5	terpinen-4-ol
14	4.8	10.5	carvone
15	5.0	38.0	unidentified ketone
16	6.0	4.8	bisabolene
17	6.6	4.4	citronellol
18	7.0	4.4	geranyl acetate

Gas-Liquid Chromatography :

The GLC of the oil was carried out using chromatograph equipped with thermal conductivity detector and 18 ft carbowax 20*M* (10%) column. The column and injection part temperatures were maintained at 160° and 200° respectively. Hydrogen was used as carrier gas (40 ml/min). Eighteen peaks obtained in the chromatogram were identified by comparing their relative retention times with those of the authentic samples recorded under identical operating conditions. The percentage of each constituent in the oil was determined by calculating corresponding peak areas. The results are given in the Table.

Thus GLC revealed the presence of seven more compounds, viz., α-pinene, myrcene, γ-terpinene, *p*-cymene, linalyl acetate, bornyl acetate and one unidentified compound in addition to those identified by chemical methods.

Acknowledgement

The authors are grateful to UGC, New Delhi for financial assistance.

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Synthesis and Pharmacology of N-Substituted-4-(*p*-Methoxyphenyl) Piperidine-2,6-diones

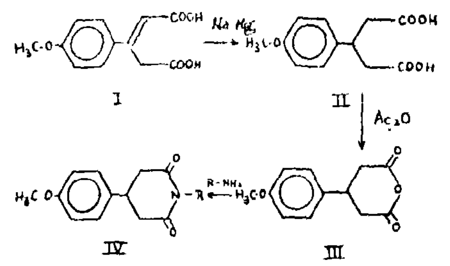
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RECENTLY various N-substituted (alkyl, cyclo alkyl and aryl)-4-arylglutarimides have been reported to exhibit antineoplastic activity[1-7]. Pyridine and pyrimidine bases are building blocks of nucleic acids and their various derivatives possess antitumor activity[8]. In view of these observations we synthesized N-heterocyclic-4-(*p*-methoxyphehyl) piperidine-2, 6-diones (IV) as possible antineoplastic agents. In these derivatives pyridine or pyrimidine residues may function as carrier groups. IVg was also prepared to incorporate glycine in the imide structure.

3-(*p*-Methoxyphenyl) glutaric acid (II), prepared by the reduction of corresponding glutaconic acid[9] (I), was treated with Ac_2O to obtain the glutaric anhydride (III). Heterocyclic amines were condensed with III at fusion temperature to furnish IVa-g. IR spectrum of IVd showed two peaks at 1690 and 1733 cm^{-1} characteristic of cyclic imide structure.



Experimental

Melting points were recorded on Gallenkamp m.p. apparatus and are uncorrected. IR spectrum was recorded on Beckmann Acculab-10 Spectrometer.

(IVa) *N-(4-Pyridyl)-4 (p-methoxyphenyl) piperidine-2,6-dione* :

III (2.18g, 0.01*M*) and 4-amino pyridine (1.04g, 0.011*M*) were mixed and heated to 170 – 180° with stirring for 30 min. The residue was crystallized from water.

m.p. 163-164°. Yield : 1.6g (53%).

Anal : Found : C, 68.61 ; H, 5.28 ; N, 9.26%

Calcd. for $C_{17}H_{16}N_2O_3$: C, 68.84 ; H, 5.43 ; N, 9.44%.

(IVg) *4-(p-Methoxyphenyl) piperidine-2, 6-dione-1-acetic acid* :

III (2.18g, 0.01*M*) and glycine (0.75 g, 0.01*M*) were fused at 180 – 190° with stirring for 15 min. The dark residue was dissolved in $NaHCO_3$ solution, and filtered. The filtrate was neutralized with HCl and the regenerated solid was crystallized with water.

m.p. 167 – 168°. Yield : 2g (71.4%).

Anal : Found : C, 60.78 ; H, 5.53 ; N, 5.13%

Calcd. for $C_{14}H_{15}NO_5$: C, 60.64 ; H, 5.45 ; N, 5.05%.

Pharmacology : Compounds IVc, b, d and e (NSC 301435 – 301438) were screened for anticancer activity *in vivo*. Compounds were injected i.p. in saline solution to male mice at doses 400, 200 and 100 mg/kg. The action of the compounds was observed by comparing the median survival time of control and test groups of animals (T/C%) in which P 388 lymphocytic leukemia was induced. The compounds failed to protect the animals from the growth of leukemia. No activity was indicated (% T/C ≯ 140). No toxicity was also observed (as % T/C ≮ 80 and no mortality). % T/C for these compounds are 100±5.

TABLE 1 —ANALYTICAL DATA OF N-SUBSTITUTED-4-(p-METHOXYPHENYL) PIPERIDINE-2,6-DIONES(IV)

No.	R	m.p. °C	Yield %
IVa	4-Pyridyl	163-164	53
IVb	6-Methyl-2-pyridyl	182-183	43
IVc	3-Methyl-2-pyridyl	141-142	28
IVd	2-Pyrimidyl	176-177	33
IVe	4-Methyl-2-pyrimidyl	184-185	32
IVf	4,6-Dimethyl-2-pyrimidyl	207-208	34
IVg	$-CH_2$-COOH	167-168	71

Elemental analyses of the compound were consistent with their composition.

Acknowledgement

Authors are grateful to Dr. Yoder, Institut Jules Bordet, Brussels, Belgium. One of the authors (SDS) is grateful to U.G C for the award of Junior Research Fellowship.

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Studies on Cycloimmonium Ylides : Synthesis of Some New 2,4,6-Triaryl Pyridines via Pyridinium Ylides

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Manuscript received 24 November 1978, revised 31 May 1980, accepted 26 July 1980

IN continuation to our previous researches[1-2] directed towards studies on pyridinium ylides, presently we wish to report herein the synthesis of some new 2,4,6-trisubstituted pyridines having phenyl, naphthyl and phenanthryl ring attached to the pyridine nucleus which have been achieved by the cyclization reaction of 3-phenanthroylmethylene pyridinium ylide with α, β-unsaturated ketones.

Experimental

Melting points were determined on a Gallen Kamp apparatus and are uncorrected. The IR spectra were recorded on a Perkin Elmer Infracord spectrophotometer in KBr phase. The NMR spectra ($CDCl_3$) were run using A-60 spectrometer using TMS as an internal standard. The products were purified by column chromatography over neutral alumina. The purity was checked by thin layer chromatography using glass plates coated with silica gel 'G' and the spots were detected by placing the tlc plates in iodine chamber.

The pyridinium salt (1) was prepared using the procedure of King *et al*[7,8].

Preparation of 2, 4, 6-triaryl-substituted pyridines (5a – n) :

A mixture of pyridinium salt (1) (3 mmol) and ammonium acetate (3g) in glacial acetic acid (20 ml) was stirred for 30 minutes. To this mixture benzylidene ketone (3a – n) (3 mmol) in glacial acetic acid (10 ml), was added dropwise during 1 hr, after which the temperature was maintained at 120° and heating was continued for additional 4-8 hr. The mixture was left overnight at room temperature and ice cold water (20 ml) was added to precipitate a solid which was separated, washed with methanol, dried and crystallized from appropriate solvent to give 2,4,6-trisubstituted pyridines (5a – n) in 40-75 percent yields (Table 1).

Results and Discussion

3-Phenanthroylmethyl pyridinium salt (1) reacts with a variety of substituted benzylideneacetophenones (3a-e), benzylidene 2-acetonaphthalenes (3f-i) and benzylidene 3-acetophenanthrenes (3j-n) in the presence of ammonium acetate and acetic acid at reflux temperature to give 2, 4-di-(substitutedphenyl)-6-(3-phenanthryl)pyridines (5a-e), 4-substitutedphenyl-2-naphthyl -6-(3-phenanthryl) pyridines (5f-i) and 2,6-di-(3-phenanthryl)-4-(substitutedphenyl)pyridines (5j-n) in 40-75 percent yields (Scheme-1).

The course of formation of pyridines from pyridinium ylide has been reported earlier[3,4]. The ylide (2), which was supposed to be formed by the dehydrohalogenation of pyridinium salt (1), attack on β-carbon atom of α,β-unsaturated ketones (3a-n), yielding new ylide intermediate, pentane-1, 5-dionyl pyridinium derivatives (4), which, in turn, underwent cyclization in the presence of ammonium acetate to give 2,4,6-tri substituted pyridines (5a-n).

The pyridines (5a-n) thus synthesized gave satisfactory elemental analysis and were new. The IR spectra (KBr) showed a characteristic absorption

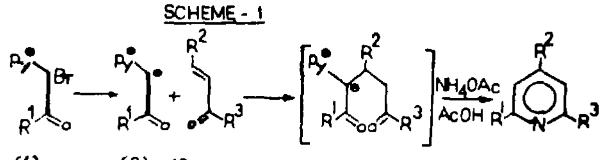
TABLE 1—PHYSICAL PROPERTIES AND SPECTRAL DATA OF 2,4,6-TRIARYL PYRIDINES (5a-n)

Compd.*	m.p. °C	Recrystn. solvent	Yield	^1H NMR ($CDCl_3$) data**			IR (KBr) data cm^{-1}		
				δ ppm	No. of protons	Assignment	C=C Stretching	C=N Stretching	C–H Stretching
5a	156-58	Py-MeOH	65	7.17-8.73m 2.48s	19H 3H	Aromatic Methyl			
5b	140-41	$CHCl_3$-MeOH	60	6.81-8.40m 2.45s	18H 3H	Aromatic methyl			
5c	108-10	Py-MeOH	65	—	—	—	1595	1503	3021
5d	142-44	Py-$CHCl_3$	75	6.83-8.55m 6.06s	18H 2H	Aromatic $-OCH_2-O$			
5e	180-82	$CHCl_3$-MeOH	55	—	—	—	1600	1546	3020
5f	178-80	Py-MeOH	65	—	—	—	1600	1570	3090
5g	135-37	$CHCl_3$-MeOH	60	7.07-8 21m	21H	Aromatic	1597	1558	3125
5h	170-72	Py-EtOH	55	6.73-8.66m 3.85d (J=4.5 Hz)	20H 6H	Aromatic Dimethoxy	— —	— —	— —
5i	170-72	Py-MeOH	50	7.80-8.44m 2.47s	22H 3H	Aromatic Methyl	— —	— —	— —
5j	150-55	$CHCl_3$-MeOH	50	7.20-8.43m 4.03s	24H 3H	Aromatic Methoxy	—	—	—
5k	107-09	Py-EtOH	60	7.50-8.44m 2.40s	24H 3H	Aromatic Methyl	—	—	—
5l	220-22	$CHCl_3$-MeOH	60	6 87-8.64m 6 03s	23H 2H	Aromatic $-OCH_2O-$	1592	1548	3058
5m	180-82	Py-EtOH	30	—	—	—	1615	1550	3140
5n	230-34	Py-MeOH	40	—	—	—	1608	1546	3006

* All compounds gave satisfactory analysis for C, H and N.
** Key words : s = singlet, m = multiplet, d = doublet.

band in the region 3100-3000 cm^{-1}, which was assigned to the C–H stretching mode of the pyridine rings. Two bands in the region 1600 cm^{-1} and 1500 cm^{-1} were assigned to the C=C and C=N vibrations of the pyridine rings. The former band appearing as a double absorption maxima near 1600 cm^{-1} seems to be a general characteristic of trisubstitution at pyridine nucleus[5,6]. The nmr

SCHEME - 1



(1) (2) (3a-n) (4) (5a-n)

1, 2, R^1 = 3-phenanthryl.
3, 4, 5a, R^1 = 3-phenanthryl; R^2 = 4-Cl.C_6H_4 ; R^3 = 4-CH_3.C_6H_4
b, R^1 = ,, ; R^2 = 2,4-Cl_2.C_6H_3 ; R^3 = 4-CH_3.C_6H_4
c, R^1 = ,, ; R^2 = 4-$NO_2C_6H_4$; R^3 = 4-Br C_6H_4
d, R^1 = ,, ; R^2 = 3,4-$O_2CH_2C_6H_3$; R^3 = 4-Br.C_6H_4
e, R^1 = ,, ; R^2 = 4-Cl.C_6H_4 ; R^3 = 4-Br.C_6H_4
f, R^1 = ,, ; R^2 = 4-Cl.C_6H_4 ; R^3 = 2-$C_{10}H_7$
g, R^1 = ,, ; R^2 = 2,4-$Cl_2C_6H_3$; R^3 = 2-$C_{10}H_7$
h, R^1 = ,, ; R^2 = 3,4-$(OCH_3)_2$ 6-BrC_6H_2 ; R^3 = 2-$C_{10}H_7$
i, R^1 = ,, ; R^2 = 4-CH_3.C_6H_4 ; R^3 = 2-$C_{10}H_7$
j, R^1 = ,, ; R^2 = 4-OCH_3.C_6H_4 ; R^3 = 3-phenanthryl
k, R^1 = ,, ; R^2 = 4-CH_3.C_6H_4 ; R^3 = ,,
l, R^1 = ,, ; R^2 = 3,4-$O_2CH_2C_6H_3$; R^3 = ,,
m, R^1 = ,, ; R^2 = 4-Cl.C_6H_4 ; R^3 = ,,
n, R^1 = ,, ; R^2 = 2,4-$Cl_2C_6H_3$; R^3 = ,,

spectra ($CDCl_3$) in general showed aromatic multiplets in the range δ 6.80 – ?.60 (Table 1).

Acknowledgement

Authors thank Director, H. B. T. I., Kanpur for providing facilities. KCG thanks UGC, New Delhi for the award of Teacher Fellowship. AKD is thankful to CSIR, New Delhi for the award of Senior Research Fellowship.

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Synthesis of Some Pyrimidinylpyrazoles and Pyrimidinyl-2-Pyrazoline-5-Ones

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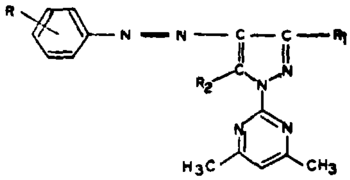
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Manuscript received 3 April 1980, accepted 26 July 1980

PYRAZOLES are known to possess various types of biological activity[1-3]. Arylazo derivatives of pyrazoles have been prepared earlier in these laboratories as possible antidiabetic agents[4,5]. In view of the important pharmacological activity displayed by the pyrimidine derivatives, it was thought of considerable interest to prepare the compounds containing both the pyrimidine and pyrazole nucleus. The present communication describes the synthesis of various 3,5-disubstituted-1-(4. 6-dimethylpyrimidin-2-yl)-4-arylazopyrazoles (I, II and III) and 1-(4,6-dimethylpyrimidin-2-yl)-3-methyl-4-arylhydrazono-2-pyrazoline-5-ones(IV).

The condensation of 2-hydrazino-4,6-dimethylpyrimidine[6] with 2, 3, 4-pentanetrione-3-arylhydrazones[4], 1-phenylbutane-1, 2, 3-trione-2-arylhydrazones[7] and 1,3-diphenylpropane-1, 2, 3-trione-2-arylhydrazones in glacial acetic acid-ethanol gave 1-(4,6-dimethyl-pyrimidin-2-yl)-3, 5-dimethyl-4-arylazopyrazoles(I). (Table 1),

TABLE 1 – 4-ARYLAZO-(4,6-DIMETHYL PYRIMIDIN-2-YL)-3,5-DIMETHYL-PYRAZOLES(I)



[I], $R_1 = R_2 = CH_3$,
[II], $R_1 = CH_3$; $R_2 = C_6H_5$,
[III], $R_1 = R_2 = C_6H_5$,

Compound No.	R	Yield %	m.p. °C
1	Hydrogen	50	98[e]
2	2-Chloro	65	142[d]
3	3-Chloro	65	112[c]
4	2-Methyl	60	150[d]
5	4-Methyl	70	160[b]
6	2-Methoxy	55	136[d]
7	2-Ethoxy	60	178[e]
8	4-Ethoxy	60	89[d]
9	4-Bromo	70	114[f]
10	2,5-Dimethyl	70	142[d]
11	3-Nitro	65	108[d]

a, red ; b, light yellow ; c, yellow ; d, brown ; e, orange yellow ; f, light greenish yellow.

The nitrogen analysis of all the compounds is consistent with the respective composition.

TABLE 2 4-ARYLAZO-1-(4,6-DIMETHYLPYRIMIDIN-2-YL)-3-METHYL-5-PHENYLPYRAZOLES(II)

Compound No.	R	Yield %	mp..* °C
1	Hydrogen	70	154
2	2-Chloro	60	207[e]
3	3-Chloro	55	170[c]
4	2-Methyl	50	155[e]
5	2-Methoxy	50	208[c]
6	3-Methoxy	45	142[d]
7	4-Ethoxy	55	120[d]
8	2,3-Dimethyl	60	267[d]
9	2 5-Dimethyl	60	110[d]
10	2,5-Dichloro	65	178[c]

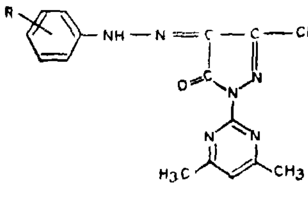
* See footnote Table 1.

TABLE 3—4-ARYLAZO-1-(4,6-DIMETHYLPYRIMIDIN-2-YL)-3,5-DIPHENYL-PYRAZOLES(III)

Compound No.	R	Yield %	m.p. °C
1	Hydrogen	50	145[c]
2	2-Chloro	55	180[e]
3	3-Chloro	60	210[c]
4	2-Methyl	50	198[d]
5	3-Methyl	55	178[e]
6	2-Methoxy	50	125[d]
7	3-Methoxy	50	146[d]
8	2-Ethoxy	50	210[c]
9	4-Ethoxy	60	185[c]
10	2,3-Dimethyl	65	205[c]

* See foot note Table 1.

TABLE 4—4-ARYLHYDRAZONO-1-(4,6-DIMETHYLPYRIMIDIN-2-YL)-3-METHYLPYRAZOLINE-5-ONES(IV)



(IV)

Compound No.	R	Yield %	m.p.* °C
1	Hydrogen	75	204[a]
2	2-Chloro	60	205[c]
3	3-Chloro	65	113[b]
4	4-Chloro	70	201[c]
5	2-Methyl	60	183[b]
6	3-Methyl	65	180[c]
7	4-Methyl	60	154[c]
8	2-Methoxy	55	220[c]
9	4-Methoxy	50	178[e]
10	3-Bromo	60	216[c]
11	4-Bromo	70	102[c]
12	4-Fluoro	65	204[c]
13	2-Nitro	65	172[d]
14	3-Nitro	55	215[c]
15	4-Nitro	70	218[c]
16	2,6-Dichloro	75	168[c]

* See foot note Table 1.

1-(4, 6-dimethylpyrimidin-2-yl)-3-methyl-5-phenyl-4-arylazopyrazoles(II), (Table 2), 1-(4,6-dimethylpyrimidin-2-yl)-3,5-diphenyl-4-arylazopyrazoles (III), (Table 3) respectively in good yields(45-70%). In a similar way, the condensation of 2-hydrazin-4,6-dimethylpyrimidine with ethyl-2,3-dioxobutyrate-2-arylhydrazones[5] resulted in the formation of 1-(4, 6-dimethylpyrimidin-2-yl)-3-methyl-4-arylhydrazono-2-pyrazoline-5-ones(IV), (Table 4) in good yields (50–75%). Some selected compounds have been assayed for the antidiabetic activity by the procedure described earlier[8]. None of the compounds showed any noteworthy activity.

1-(4,6-dimethylpyrimidin-2-yl)-3,5, dimethyl-4-phenylazopyrazole(I, 1) :

A solution of 2,3,4-pentanetrione-3-phenylhydrazone (2.04g, 0.01 mole) in glacial acetic acid (50 ml) was added to a hot solution of 2-hydrazino-4,6-dimethylpyrimidine (1.38g, 0.01 mole) in ethanol (50 ml). The resulting mixture was heated at reflux for 3 hr. It was cooled. The crystals of (I, 1) obtained were crystallized from dimethylformamide. Yield : 1.5g, 50% : m.p. 98° ; Found : C, 66.20 ; H, 5.58 ; N, 27.30 ; $C_{17}H_{18}N_6$ requires C, 66.66 ; H, 5.88 ; N, 27.45%.

1-(4, 6-dimethylpyrimidin-2-yl)-3-methyl-4-phenylhydrazono-2 pyrazoline-5-ones(IV, 1) :

A solution of ethyl-2,3-dioxobutyrate-2-phenylhydrazone (2.36g, 0.01 mole) in glacial acetic acid (30 ml) was added to hot solution of 2-hydrazino-4, 6-dimethylpyrimidine (2.76 g, 0.02 mole) in ethanol (50 ml) with stirring. The resulting mixture was heated at reflux for 2 hr. On cooling crystals separated out which were crystallized from dimethylformamide. Yield : 2.3g, 75%, m.p. 204° ; Found : C, 62.00 ; H, 4.90 ; N, 27.40. $C_{16}H_{16}N_6O$ requires C,62.33 ; H, 5.19 ; N, 27.27%.

Acknowledgement

One of the authors (R.S.) thanks the Council of Scientific and Industrial Research, India for the award of a Senior Research Fellowship.

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5-Nitro-4(2)-[4-Oxo-3*H*-Quinazolin-3-yl]-benzylidenemalonylureas as Antibacterial Agents

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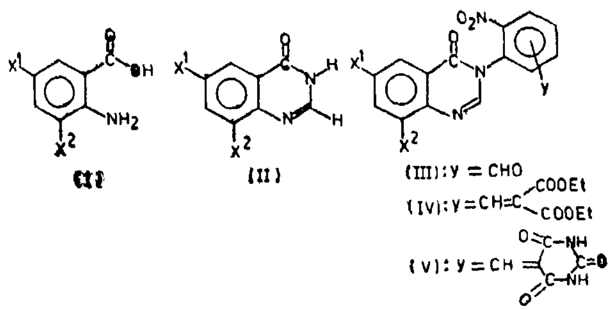
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Manuscript received 23 March 1979, revised 30 July 1979, accepted 25 October 1979

THE title compounds(v), some of which have been found to be good antibacterial agents, are synthesised by condensation of 5-Nitro-4(2)-[4-oxo-3*H*-quinazolin-3-yl]-benzaldehydes (III) successively with diethylmalonate and with urea. The quinazolone moeity has been shown to possess various antimicrobial activities[1,2]. Various urea derivatives have been found to be bacteriostatic[3-6] and antibacterial[7] agents. Further, the antimicrobial action of some aryl nitro compounds is well known[8]. Therefore, it was thought proper to synthesise the title compounds having all these three moeities and to test their activity against the bacteria *S. aureus*.

Experimental

The quinazolones(II) were synthesised by reacting anthranilic acids[9,10] (I) with formamide, following the conventional method[11]. The quinazolones (II) were reacted with 3-nitro-4 (2)-chloro benzaldehydes to obtain the aldehydes (III), which were subjected to condense with diethylmalonate and the resultant products (IV) were refluxed with ureas and sodium ethoxide in ethanol, when malonyl ureas (V) resulted in



The m. ps. were taken in open capillaries, in sulphuric acid bath. All compounds gave satisfactory elemental analysis data. The structure of the compounds was further confirmed by the IR spectroscopic studies. The IR spectra were taken in KBr phase.

Important IR (taken in KBr phase) peaks of the compounds (III) were ~1670 cm^{-1} (quinazolonyl O ‖ C-N group), ~1560 cm^{-1}, ~1380 cm^{-1} (aromatic C-NO_2) and ~1700 cm^{-1} ~2830 cm^{-1}, ~2750 cm^{-1} (aryl CHO). The absence of a peak between 3200-3500 cm^{-1} in this compound shows the utilization of active 'H' at position-3 of quinazolone during the formation of (III).

The IR spectrographs of compounds (IV) include the peaks at ~1670 cm^{-1}, ~1560 cm^{-1}, ~1380 cm^{-1} and ~1720 cm^{-1}. The absence of peaks at ~1700 cm^{-1}, ~2830 cm^{-1}, ~2750 cm^{-1}, previously found in the IR of (III), indicated for the utilization of 'CHO' group during this step. The peak at ~1720 cm^{-1}, further confirmed the formation of diethyl benzylidene malonate group in the compounds (IV).

The IR spectrographs of the compounds (V), displayed the important peaks at ~1670 cm^{-1}, ~1560 cm^{-1}, ~1380 cm^{-1} and ~3425 cm^{-1} (N-H stretch) and ~1630 cm^{-1} (for C=O group of malonyl urea moeity). The absence of peak at ~1720 cm^{-1} previously found in (IV), indicated for the utilization of α-β-unsaturated ester group and the peak at ~3425 cm^{-1} and at ~1630 cm^{-1} indicated the formation of malonyl ureas in compounds (V).

5-Nitro-4(2)-[4-oxo-6, 8-disubstituted-3H-quinazolin-3-yl]-benzaldehydes (III) :

3-Nitro-4(2)-chlorobenzaldehyde (0.01 mole) and the appropriate quinazolone (0.0 mole) in dry ethanol (20 ml) and pyridine (0.5 ml) were refluxed on a water bath for 1 hr. under anhydrous conditions. The mixture was then poured in ice and conc. HCl mixture (2 : 1 ; w/v). The solid, so separated was filtered and recrystallised with ethanol/water ; yield 70-80%. The relevant data are given in Table 1.

TABLE 1 – MELTING POINTS (IN °C)* OF THE BENZALDEHYDES(III), BENZYLIDENE MALONATES(IV) AND THE MALONYLUREAS(V).

Sl. No.	X¹	X²	Position of 'y'	Compound (III)	Compound (IV)	Compound (V)
a.	H	H	4	170	105	194
b.	H	Br	4	260	252	282
c.	Br	Br	4	252	245	197
d.	H	I	4	250	247	225
e.	H	H	2	235	220	244
f.	H	Br	2	253	250	268
g.	Br	Br	2	282	240	205
h.	H	I	2	262	254	249

*M.P.S. were determined in open capillaries, hence uncorrected.

5-Nitro-4(2)-4-[oxo-6,8-disubstituted-3H-quinazolin-3-yl]-diethyl malonate(IV) :

Upon refluxing for 3-4 hrs the diethyl malonate (0.01 mole) and the corresponding (III) (0.01 mole) in acetic anhydride (10 ml) under dry conditions and then pouring the mixture in ice with constant stirring, a

solid mass separated after 24 hrs. The solid was filtered and recrystallised from alcohol; yield-about 60-70%. The relevant data are given in Table 1.

5-Nitro-4(2)-[4-oxo-6,8-disubstituted-3H-quinazolin-3-yl]-benzylidene malonylureas(V) :

A mixture of (IV) (0 01 mole) urea (0.01 mole) and ethanolic NaOEt (0.01 mole) was refluxed for 6-7 hrs on a steam bath and subsequently refluxed on oil bath for 16 hrs at 110-115°. The mixture then treated with 20 ml in hot dil. HCl and was kept in an ice-chest overnight. The solid was filtered and recrystallised from ethyl alcohol. The yield was about 60-70%. The relevant data are given in Table 1.

Antibacterial screening : All the compounds (V) were screened out for their antibacterial activity against *S. aureus*, using the method of Verma and Nobels[12]. Zone of inhibition to these bacteria ranged between 5-15 mm for compounds Va, Vd, Ve, Vg and Vh. Compounds Vb, Vc and Vf were inactive. Compound Ve was found to be the best active (15 mm sterilization zone).

Acknowledgement

Thanks are due to CSIR, New Delhi for the award of a S.R.F. to one of us (R.K.S.).

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Synthesis and CNS Activity of 1-(5′-Alkyl, 1′, 3′, 4′-thiadiazol-2′-yl), 2-methyl, 4-arylidene-imidazol-5-ones.

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Manuscript received 14 February 1979, revised 30 July 1979, accepted 25 October 1979

FIFTEEN new thiadiazolyl imidazolone derivatives (III) have been synthesised by the condensation of some 2-methyl, 4-arylidene azalactones (I) with 2-amino, 5-alkyl-thiadiazoles (II) in pyridine. The 2-amino-thiadiazole[1-5] and imidazolone[6-8] derivatives have been reported to possess various CNS activities. It was thought worthwhile to investigate whether the compounds having both imidazolone and thiadiazole moieties can have better pharmacological results. The reported MAO-inhibitory activity in imidazolone nucleus[9,10], guided the idea that the mechanism of action of the aforesaid compounds on parkinsonian features could be dopaminergic, therefore their MAO-inhibitory activity was also tested.

2-Amino, 5-alkyl-1, 3, 4-thiadiazoles : These were synthesised by the method of Funatsukuri *et al*[11].

2-Methyl, 4-arylidene-azlact-5-ones : These were synthesised using the procedure of Vogel[12], Herbert and Shemin[13], Dakin[14] and Nlender and Ziering[15].

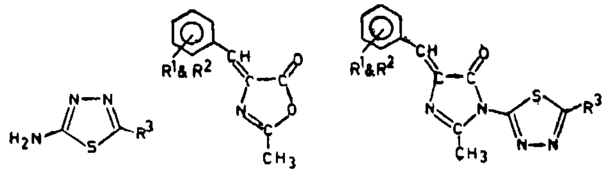
1-(5′-Methyl, 1′, 3′, 4′-thiadiazol-2′-yl)-2′-methyl-4-(p-methoxy benzylidene)-imidazol-5-one :

2-Amino, 5-methyl 1, 3, 4-thiadiazole (0.01 mole) and 2-methyl, 4-(*p*-methoxy benzylidene)-azlact-5-one (0.01 mole) were taken in pyridine (15 ml) and the mixture was refluxed for about 6 hr on a sand bath. The excess of pyridine was distilled off at reduced pressure and the residue was cooled at room temperature. It was then poured in a mixture of 50 ml conc. HCl and 50 g ice and left overnight. The solid seperated was filtered and recrystallised twice with ethanol and dried. Yield 70%; m.p. 118-19°. IR(KBr) 1660 cm^{-1} (for C=C stretch trisubstituted); 1680cm^{-1} (for ring N–C(=O)– group of imidazolone moiety); 1640 cm^{-1} (for ring C=N bonding). Similarly other 1-(5′-alkyl-1′,3′,4′-thiadiazol-2′-yl)-2-methyl-4-arylidene imidazol-5-ones were prepared and are described in Table 1.

Pharmacology : All the compounds were screened for CNS activity on albino mice of either sex. Acute toxicity test was also done and the ALD_{50} of these compounds was also determined following the method of Weil[16]. ALD_{50} are given in Table 1.

The compounds are relatively nontoxic. Compound Nos. 5,12,13 produced piloerection and stimulations

TABLE 1—1-(5′-ALKYL, 1′,3′,4′-THIADIAZOL-2′-YL), 2-METHYL, 4-ARYLIDENE IMIDAZOL-5-ONES(III)



(I) (II) (III)

Compd. No.	Molecular formula	R_1	R_2	Melting* points (°C)	S% Calcd.	S% Found	N% Calcd.	N% Found	ALD_{50} (mg/kg wt of mice)
	$R_3=CH_3$								
1.	$C_{14}H_{12}ON_4S$	H	H	164	11.27	11.02	19.71	19.52	>1000
2.	$C_{14}H_{11}ON_4SCl$	H	*p*-Cl	219-20	10.04	10.23	17.58	17.29	>1000
3.	$C_{15}H_{14}O_2N_4S$	H	*p*-OCH_3	218-19	10.17	10.22	17.80	17.72	1000
4.	$C_{14}H_{12}O_2N_4S$	H	*o*-OH	211-12	10.66	10.39	18.66	18.32	825
5.	$C_{15}H_{14}O_3N_4S$	*p*-OH	*m*-OCH_3	158-59	9.69	9.92	16.96	17.23	1000
	$R_3=C_2H_5$								
6.	$C_{15}H_{14}ON_4S$	H	H	187	10.73	10.92	18.79	18.29	825
7.	$C_{15}H_{13}ON_4SCl$	H	*p*-Cl	243-44	9.62	9.39	16.84	17.12	>1000
8.	$C_{16}H_{16}O_2N_4S$	H	*p*-OCH_3	165-66	9.75	9.65	17.07	17.43	681
9.	$C_{15}H_{14}O_2N_4S$	H	*o*-OH	235-36	10.19	10.32	17.83	17.53	825
10.	$C_{16}H_{16}O_3N_4S$	*p*-OH	*m*-OCH_3	215	9.30	9.62	16.28	16.58	681
	$R_3=C_3H_7$								
11.	$C_{16}H_{16}ON_4S$	H	H	174-75	10.25	10.45	17.94	17.64	>1000
12.	$C_{16}H_{15}ON_4SCl$	H	*p*-Cl	188	9.23	9.46	16.16	16.34	681
13.	$C_{17}H_{18}O_2N_4S$	H	*p*-OCH_3	196-97	9.36	9.12	16.37	16.49	681
14.	$C_{16}H_{16}O_2N_4S$	H	*o*-OH	184-85	9.75	9.49	17.0 7	17.34	825
15.	$C_{17}H_{18}O_3N_4S$	*p*-OH	*m*-OCH_3	169-70	8.93	9.02	15.64	16.21	>1000

* The melting points were taken in open capillaries and are uncorrected. Yield ranged between 60-70%.

on the CNS. Compound nos. 1, 2, 6 and 10 increased the rate of breathing at all doses. SMA and reactivity was increased by all the compounds at all doses.

These compounds were also tested for anti-tremorine activity but no significant results were obtained. They were also screened for their *in-vivo* mono-amine oxidase inhibitory activity against 'Reserpine' induced activity. All the compounds reversed the stimulating effects of reserpine at 3 hr after the dose given. Howevr, the activity was negative at 18 hr observations after the drug administration.

Acknowledgement

Thanks are due to Prof. B. N. Dhawan, Head of Pharmacology Department, C.D.R.I., Lucknow for pharmacological screenings.

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Chemical Constituents of the Stem bark of *Elaeodendron glaucum* Pers

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Manuscript received 24 July 1979, revised 25 February 1980, accepted 26 July 1980

ELAEODENDRON glaucum Pers (Celastraceae) is generally grown for its medicinal importance[1]. The leaves are found to have a sternutatory and fumigatory action. They are also used as a snuff to relieve headache. The gum obtained from the plant dissolves in water to give an adhesive. A survey of literature revealed no work on this plant and hence an investigation of its stem bark was undertaken. We have obtained n-octacosanol, friedelin, β-sitosterol, betulonic acid, 23-hydroxy betulin, β-sitosterol-β-D-glucoside from the benzene extract and dulcitol from the alcohol extract of the stem bark.

The finely ground stem bark was extracted thoroughly with benzene followed by extraction with alcohol.

Benzene Extract :

This was concentrated under vacuum when a brown mass was obtained which was chromatographed over silica gel.

n-*Octacosanol* : Elution of the column with pet. ether-benzene (3:1) afforded n-octacosanol, white granules m.p. 83-4° (EtOAc), $C_{28}H_{58}O$, I.R., ν_{max}^{nujol} : 3230, 730 and 720 cm^{-1} ; acetate (Ac_2O/pyr.), m p. 64-5°.

Friedelin : Elution of the column with pet. ether-benzene (1:1) furnished friedelin, white microneedles, m p. 258-60° (pet. ether), $C_{30}H_{50}O$, M^+ 426, I.R., ν_{max}^{KBr} : 1720 cm^{-1} ; oxime, m.p. 2 0-2°. It was identical (mmp, TLC and IR) with an authentic sample.

β-Sitosterol : Elution of the column with benzene yielded β-sitosterol, m p. 136-7° (EtOH); acetate (Ac_2O/pyr.) 125-6°, identical (mmp and TLC) with an authentic sample.

Betulonic Acid : Elution of the column with benzene-ethyl acetate (1 : 1) furnished white crystals of betulonic acid m.p. 251-3° (C_6H_6 : EtOAc), found : C, 79.05 ; H, 10.25% $C_{30}H_{46}O_3$ requires C, 79.25 ; H, 10.20%, I.R., ν_{max}^{KBr} ; 3100 (broad), 1710, 1690 cm^{-1} ; methyl ester (CH_2N_2), m.p. 162-3°, identical (mmp, TLC and IR) with an authentic sample.

23-Hydroxy betulin : Further elution of the column with benzene-ethyl acetate (1:1) yielded white microneedles of 23-hydroxybetulin, m.p. 256-8° (C_6H_6 : EtOAc), found : C, 78.80 ; H, 10.70% $C_{30}H_{50}O_3$ requires C, 78.55 ; H, 10.99%. I.R., ν_{max}^{KBr} : 3380 cm^{-1} ; acetate (Ac_2O/pyr.), amorphous, uncrystallizable, acetate group determination showed the presence of three hydroxy groups in the compound. Identical (mmp, TLC and IR) with an authentic sample.

β-Sitosterol-β-D-glucoside : Elution of the column with ethylacetate-methanol (1:1) furnished white microneedles of β-sitosterol- β - D - glucoside, m.p. 290-2° (MeOH), found : C, 72.79 ; H, 10.23% $C_{35}H_{60}O_6$ requires C, 72.91 ; H, 10.41%. I.R., ν_{max}^{KBr} : 3400 cm^{-1}; acetate, m p. 166°. On acidic hydrolysis, β-sitosterol, m.p. 135-7°, identical (mmp and TLC) with an authentic sample and glucose (Co-paper chromatography) were obtained.

Alcohol Extract :

Dulcitol : The concentrated extract when kept in a refrigerator for 48 hours deposited a white solid. On recrystallisation, it yielded dulcitol, white shining crystals, m.p. 185-6° (50% EtOH) ; hexaacetate (Ac_2O/pyr.), m.p. 166-8°. It was identical (mmp and paper chromatography) with an authentic sample.

Acknowledgement

We are grateful to the C.S.I.R., New Delhi, for the award of Junior Research Fellowship to one of us (R. P.).

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Chemistry of *Acacia concinn* and *A. caesia* Bark

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Manuscript received 30 July 1979, revised 4 March 1980, accepted 26 July 1980

ACACIA concinna D. C., popularly known as *Shikakai*, is a prickly scandent bush occurring throughout tropical forests of India. Since its pods are used extensively as detergent, they are often confused with soap-nut (*Sapindus mucorossi*) because of their similar properties[1].

The pods yielded saponin, the sapogenins of which were characterised as acacic acid lactone, machaerinic acid and its lactone by Anjaneyulu *et al*[2] in contradiction to the observation of Varshney *et al*[3,4] who reported only acacic acid.

Certain tribes in Nilgiris (S. India) also use its bark for cleaning hair[5]. Literature survey revealed that no work has been done on the bark, therefore, a systematic chemical examination of this part was undertaken. The bark yielded saponin which was found to possess spermicidal activity[6].

Acacia caesia Willd., a sister species of *A. concinna* is a large climbing shrub distributed in Gujarat, Konkan and Western Ghats of Bombay to Anamalais[7]. The bark is reported[8] to yield stigmasterol, a triterpene alcohol and an aliphatic hydroxy compound.

The bark on reinvestigation did not yield any saponin. The absence of saponin would support the contention of Gamble[9] that *A. caesia* is either one of the varieties of *A. intsia* or a separate species but not synonymous[10] with *A. intsia* which yields[11] saponin with acacic acid as the sapogenin.

Experimental

The powdered bark of *A. concinna* was sequentially extracted with alcohol and *n*-hexane. The alcoholic extract was separated into ether soluble and insoluble fractions. The ether soluble fraction was combined with the *n*-hexane extract and subjected to column chromatography over alumina to yield, *hexacosanol*, m. p. 80° ; $C_{26}H_{54}O$; acetate, m. p. 64°, indentified through mixed m. p., co-TLC and superposable IR spectra ; *α-Spinasterone*, m. p. 164-165° ; $C_{29}H_{46}O$ (Found : C, 84.79 ; H, 11.32%. Calcd. C, 84.88 ; H, 11.22%) ; ν_{max}^{KBr} 1710, 997 cm^{-1} ; MS, m/e 410 (M^+), 367, 298, 271 and 229, characterised by mixed m. p., co-TLC and superposable IR spectra with an authentic sample and its reduction ($LiAlH_4$) to α-spinasterol, m. p. 164-165° ; *Lupeol*, m. p. 190-192° ; $C_{30}H_{50}O$; M^+ 426 ; ν_{max}^{KBr} 3390, 1639, 880 cm^{-1} ; acetate, m. p. 210-212° ; M^+ 468, identified as lupeol by direct comparison with an authentic sample in regard to mixed m. p., co-TLC and superposable IR spectra ; *α-Spinasterol*, m. p. 164-166° ; $C_{29}H_{48}O$; M^+ 412 ; ν_{max}^{KBr} 3425, 965 cm^{-1} ; acetate, m. p. 179-181° ; $C_{31}H_{50}O_2$ (Found : C, 81.80 ; H, 11.28%. Calcd. C, 81.95 ; H, 11.01%), confirmed through mixed m. p., co-TLC, superposable IR spectra with an authentic specimen and its oxidation (CrO_3/Py) to α-spinasterone, m. p. 164°.

The ether insoluble fraction on processing yielded an amorphous saponin which on hydrolysis (2% alcoholic H_2SO_4, w/v) gave (i) *Lupeol*, m. p. 189-190° ; (ii) *α-Spinasterol*, m. p 160-162° and (iii) *Acacic acid lactone*, m. p. 254-256° ; $C_{30}H_{46}O_4$ (Found : C, 76.15 ; H, 10.97%. Calcd. C, 76.55 ; H, 9.85%) ; ν_{max}^{KBr} 3663, 3448, 1767, 1650, 980 cm^{-1} ; MS, m/e 470 (M^+), 452, 263, 244, 207 , diacetate, m p. 232-234° ; ν_{max}^{KBr} 1780, 1730, 1242 cm^{-1} ; M^+ 554. Acacic acid lactone and acacic acid lactone diacetate were confirmed through mixed m. p., co-TLC, superposable IR spectra with authentic specimens. The sugars were identified through co-PC as glucose, arabinose and rhamnose.

The occurrence of lupeol and α-spinasterol as glycosides was established by running TLC of the saponin against authentic samples of lupeol and α-spinasterol when the plate (TLC) did not show the presence of these compounds in the saponin.

The bark of *A. caesia* on similar processing (*ut supra*) yielded lupeol, α-spinasterol and stigmasterol but no saponin.

Spermicidal activity of the Saponin :

One percent solution of the saponin was prepared in the Sorensen's isotonic phosphate buffer (*p*H 8.0) containing 17% glucose and 0.38% NaCl for maintaining good sperm motility as recommended by Blackshaw and Emmens[12]. The required percentage of saponin was obtained by successive increment of addition of the 0.2 ml of buffer solution. Human semen was diluted to the extent to give an average count of 4-6 motile spermatozoa per high power field (h.p.f.) of microscope. The tests were performed at 37° after every addition of 0.2 ml solution of saponin and after a gap of a minute, the number of motile spermatozoa were counted under h.p.f. of microscope. The maximum activity was observed at 0.004% dilution.

Acknowledgement

Thanks are due to Prof. L. Ramachandra Row for the authentic samples of acacic acid lactone and its diacetate.

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Hydrocarbons Alcohols and Phytosterols from the Leaves of *Daucus carota*, Nantes**

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Manuscript received 24 September 1979, revised 30 May 1980, accepted 26 July 1980

LEAVES (900 gm) of *Daucus carota*, Nantes (Umbelleferae) (commonlly known as Pahari Gajar) collected from the surroundings of Aligarh district were air-dried, powdered and extracted with hot light petroleum (60-80°). A total of 18.6 gm. (2.06%) extract was obtained, which was subjected to chromatographic separation over neutral activated alumina (30 fold excess).

Elution with light petroleum (60-80°) yielded a colourless waxy product (300 mg), m. p. 57-58° (acetone), TLC-homogeneous (Silica gel-2% $AgNO_3$). I.R. spectrum indicated the presence of *n*-alkanes with a long chain. This fraction was then analysed by gas liquid chromatography which represented the homologous series of *n*-alkanes C_{15}-C_{39} with maximum occurrence of C_{29} (19.8%), C_{27} (14.3%), C_{31} (12.6%) and C_{33} (10.0%) (Table 1). Odd carbon *n*-alkanes prevailed in higher members only of the series whereas the quantitative preponderance of odd-carbon *n*-alkanes in the lower ones was not so significant[1]. Some other hydrocarbons (mono methyl branched) were also present in small amounts[2].

**Partly presented in 66th Session of Indian Science Congress Association held at Hyderabad, Jan. 1979.

TABLE 1—COMPOSITION OF *n*-ALKANES AND FREE ALCOHOLS+

No. of C-atoms	*n*-alkanes %	free alcohols %
15-21	traces	—
22	0.5	1.2
23	0.6	0.3
24	1.4	10.4
25	3.0	1.3
26	4.8	34.8
27	14.3	2.4
28	9.1	41.0
29	19.8	1.6
30	7.4	5.2
31	12 6	—
32	6.1	—
33	10.0	—
34	3.0	—
35	2.3	—
36	0.5	—
37 38,39	traces-	—

+According to GLC analysis.

Further elution with light petroleum : benzene (1:1) gave a mixture of alcohols (275 mg). This fraction on GLC analysis exhibited a homologous series of primary alcohols (C_{22}-C_{30}) with maximum occurrence of C_{28} (41.0%), C_{26} (34.8%) and C_{24} (10.4%) (Table 1). Even alcohols prevailed as usual[3,4]. From this mixture only *n-hexacosanol*, m.p. 77-78° (Lit[5]. m.p. 79.5°) could be crystallised from methanol (TLC-homogeneous). It was characterised by preparation of its acetate[6] (m.p. 64-65°) and by direct comparison with authentic specimen (m.m.p., co-TLC).

Elution with benzene gave the sterol fraction which on crystallisation from methanol gave shining crystals 200 mg), m.p. 137-40°, TLC-homogeneous (Silica gel-5% $AgNO_3$, several solvent systems). Spectral data indicated it to be a mixture of sterols which could be separated and identified by combined GC-MS. The trimethylsilyl ethers were found to contain mainly two components with two other minor constituents and were identified by direct comparison of GLC retention

TABLE 2—COMPOSITION OF PHYTOSTEROLS

Compound	RRT	Molecular ion	% of sterols			Identity
1	1.00	458	3	27C	5	Cholesterol
2	1.29	472	5	28C	5	Campesterol*
3	1.36	484	45	29C	5,22	Stigmasterol*
4	1.59	486	47	29C	5	β-sitosterol*

*(or C_{24} epimer as neither GLC nor MS can distinguish between C_{24} epimers).

times and mass spectra[7,8] with those of authentic specimens ran under identical GC-MS conditions. The results are summarised in Table 2.

Acknowledgement

The authors are grateful to Dr. S. C. Gupta, Principal and Dr. Mukat Behari, Head of the Chemistry Department, S. V. College, Aligarh for providing facilities. Sincere thanks are due to Prof. M. Streibl, Institute of Organic and Biochemistry, Prague for GLC analysis and to Lord Corporation Erie, PA (USA) for I.R. spectra. Thanks are also due to U.G.C. (New Delhi) for financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1047-1049

Determination of Stability Constants of 2-Hydroxy-1-Naphthalidene-2′-Methyl-4′-Nitro-Aniline Complexes with Y^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+} and Dy^{3+}

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Manuscript received 2 January 1979, revised 24 January 1980, accepted 26 July 1980

"Potentiometric studies have been carried out on metal complexes of Y^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+} and Dy^{3+} with 2-hydroxy-1-naphthalidene-2′-methyl-4′-nitroaniline. The dissociation constants (pK_1+pK_2) of the reagent and the formation constants of its metal complexes have been determined by Bjerrum's method at 25°±0.1° and at an ionic strength 0.1*M* in 75 : 25 percent (v/v) dioxan-water medium. The validity of Born's relation was examined by studying the plot of Z^2/r vs log k values of rare earth complexes of the ligand.

In the present communication the successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-2′-methyl-4′-nitroaniline with various trivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum *p*H titration technique as adopted by Irving and Rossotti[1].

The Corning Model 12, a precision research *p*H meter with combined glass electrode and a calomel reference electrode was used for *p*H measurements. The calomel electrode was replenished with the supplied saturated KCl solution from time to time. Both electrodes dip into the titrating mixture, without vitiating any results. The meter has an arrangement for normal and expanded scale. The changes in the *p*H can be measured with an accuracy of 0.005 *p*H unit.

Experimental

The ligand 2-hydroxy-1-naphthalidene-2′-methyl-4′-nitroaniline was prepared by dissolving 10 gm of 2-hydroxy-1-naphthaldehyde (Fluka) in 50 ml of absolute ethanol. To this was added equimolar quantity of *o*-methyl-*p*-nitroaniline. This reaction mixture was refluxed on a water bath for half an hour. After cooling, the solution was filtered to get the crude product, which was repeatedly crystallised from alcohol to get analytically pure compound. The m.p. observed was 191°.

The dioxan used for experimental work was purified by the method described by Vogel[2]. Distilled water redistilled over alkaline potassium permanganate and made free from carbon dioxide by boiling was used throughout the investigation.

The medium of titration was 75 : 25 percent dioxan-water (v/v) mixture. Sodium perchlorate was added to maintain a constant ionic strength. The titrations were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through the solutions. The free acid, the free acid plus the ligand and the mixture of metal ion containing the acid plus the ligand were titrated against standard carbonate free sodium hydroxide. Metal ion solutions of Yttrium Gadolinium and Neodymium were prepared by taking the metal nitrates of A.R. grade. Metal ion solutions of Dysprosium, Praseodymium and Lanthanum were prepared by taking the metal carbonates of A.R. grade. All metal nitrates and carbonates were supplied by S.D. Lab. Chem. Industry, Bombay. All these were standardised complexometrically[3] by EDTA titrations. All the measurements were carried out at 25°±0.1°.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1.07*M*) solution :

(i) 5 ml of (0.16*M*) $HClO_4$+5 ml of (0.64*M*) $NaClO_4$+30 ml of dioxan.

(ii) 5 ml of (0.16*M*) $HClO_4$+5 ml of (0.64*M*) $NaClO_4$+requisite amount of reagent accurately weighed to give 0.004*M* reagent concentration in the final solution +30 ml of dioxan.

(iii) 5 ml of (0.64*M*) $NaClO_4$+5 ml of metal salt (0.008*M*) solution in (0.16*M*) $HClO_4$+the requisite amount of the reagent accurately weighed to give 0.004*M* reagent concentration in the final solution +30 ml of dioxan.

The experimental method of Irving and Rossotti[1] was applied to find out the values of $\bar{n}$ and *p*L. The titrations were performed in duplicate to test for the reproducibility.

Results and Discussion

It may be pointed out here that the ligand used in this study did not undergo hydrolysis under the experimental conditions described. This was indicated by rapid attainment of equilibrium during the titration and by the absence of any significant drift in the pH even after one hour.

In the ligand it is the phenolic (OH) group that takes part in the complex formation and the ligand behaves as monoprotoic.

From the titration curves using the solutions (i) and (ii), $\bar{n}_A$ values at various 'B' values (pH meter readings), were calculated and a curve between 'B' and the corresponding $\bar{n}_A$ values was plotted (Fig. 1). The value of pK_1^H was evaluated by half integral method as well as from the plot of log $\left[\frac{\bar{n}_A}{1-\bar{n}_A}\right]$ vs 'B' (Fig. 2). Both these values agree quite well.

From the titration curves of solutions (ii) and (iii) $\bar{n}$ and pL value were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of the metal complexion equilibria. From this log K_1 and log K_2 values were evaluated by half integral method. Since the difference between the log K_1 and log K_2 values was found to be less the 1.78 log unit, the same were calculated by least square method.

The most representative values as calculated by the least square method are recorded in Table 1. The order of stability of the trivalent metal chelates was found to be $Y^{3+} > Nd^{3+} > Gd^{3+} > La^{3+} > Dy^{3+} > Pr^{3+}$.

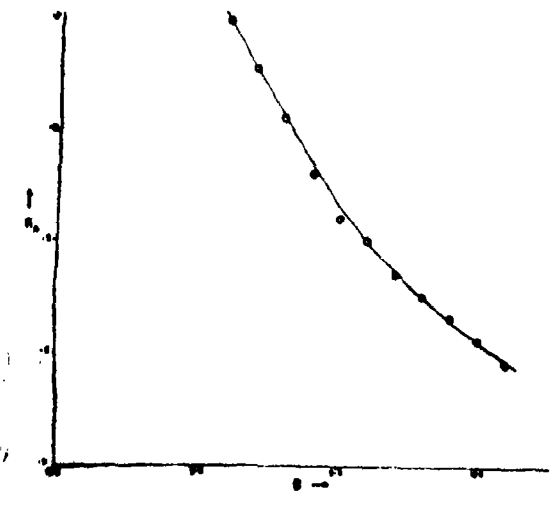


Fig. 1. Formation curve of 2-Hydroxy-1-Naphthalidene-2'-Methyl-4'-Nitroaniline. Plot of $\bar{n}_A$ vs B.

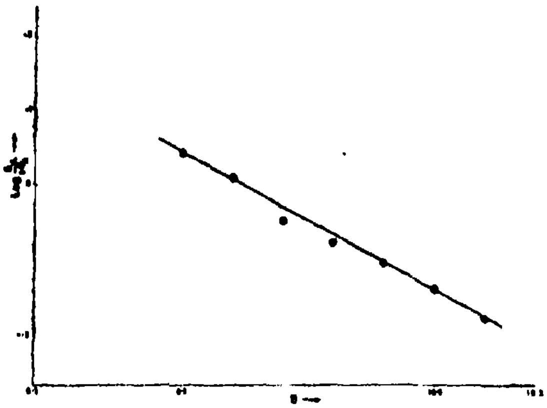


Fig. 2. 2 Hydroxy-1-Naphthalidene-2'-Methyl-4'-Nitroaniline Plot of log $\frac{\bar{n}_A}{1-\bar{n}_A}$ vs B

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES*

$t = 25°C$ $\mu = 0.1$

Cations	H^+	Y^{3+}	La^{3+}	Pr^{3+}	Nd^{3+}	Dy^{3+}	Gd^{3+}
log K_1	9.6	7.00	6.20	5.98	6.67	6.02	6.39
log K_2	—	5.92	5.09	4.75	6.32	5.80	5.06

* For proton association (H^+), K_1 corresponds to the species LH, while for metal ions K_1 and K_2 correspond to the species ML_1 and ML_2 respectively.

The rare earth metal ions differ from each other in the number of electrons in the 4f orbitals which are effectively shielded from the interaction with ligand orbitals by electrons in 5s and 5p orbitals. Hybridization would involve normally unoccupied higher energy orbitals (e.g. 5d, 6s, 6p) and this may be expected to occur with the most strongly coordinated ligands. Rare earths, therefore, normally form ionic compounds. The possibility of covalent interaction, however, cannot be completely excluded as reported, in the case of acetylacetone chelates of rare earths[4].

If the bonds are ionic, the Born relation $E = \frac{Z^2}{2r}\left[1 - \frac{1}{D}\right]$ should hold for the energy change on complexation of a gaseous ion of charge 'Z' and radius 'r' in a medium of dielectric constant 'D'. Since the stability constant is related directly to this energy, the log K values should increase linearly with Z^2/r.

The plots of Z^2/r vs log K_1 values of the rare earth complexes do not exhibit any linear increase of log K_1 with increase in Z^2/r. The probable explanation of non-linearity could be that the

assumption about ionic character of metal-ligand bond on which the linearity relation is based is not valid. The other probable causes are (i) coordination number of metal ion greater than six, and (ii) steric factor.

Acknowledgement

The authors wish to record their sincere thanks to Dr. D. G. Vartak, B. A. R. C., Bombay, for his valuable suggestions.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1050-1053

Reactions of Nickel(II) with Acid and Base Saturated Montmorillonites

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Manuscript received 7 November 1979, accepted 22 December 1979

The effects of time, pH and temperature on the interaction of nickel with H-, Na- and Ca- saturated montmorillonites have been investigated. Maximum adsorption occurs at pH 6 while before and after it (pH 6) adsorption declines. The adsorption increased rapidly and then slowly with increase in the time of interaction. The values of rate constants and the half times of reaction suggested an exchange process controlled by film and particle diffusion. The inferences were confirmed from the nature of adsorption isotherms. Temperature affected the adsorption with exothermic nature of interactions. The activation energy of adsorption of nickel on Na- and Ca-, montmorillonite was 10 2 and 10.6 k cal mole respectively.

AMONG the heavy metals used as micronutrients nickel salts especially nickel chloride has been recognised as a valuable fertilizer and fungicide[1]. A little work on the interaction of Ni(II) with clays and soils has been reported so far. The adsorption of Ni(II) in soils is affected by *p*H, organic matter and oxidation-reduction status of soils. The study of interaction of Ni(II) ions with clay minerals has been increasing in recent years[2]. Hathway and Lewis[3] by electronic absorption spectra of Ni(II) adsorption on silica gel reported that Ni(II) exists on the surface in a chemical form similar to that found in solution, Dugger *et al*[4] have reported the thermodynamic parameters for adsorption of Ni(II) on silica and Swartzen-Allen and Matijevic[5] have reviewed the quantitative aspect of Ni(II) adsorption.

Montmorillonite is an important constituent of basaltic vertisol soils which occur so widely all over the world. The mineral possesses a high cation exchange capacity and has been known to provide heterogeneous chemically reactive spots on its surface in the form of exchangeable cations, sorbed water cations, hydroxyl groups and lattice surface oxygens.

The primary objective of this work is to investigate the interaction and mechanism of adsorption of Ni(II), a typical fungicide on suspended montmorillonite particles in their acid and base saturated forms.

Experimental

The bentonite used in these studies was obtained from Akli in Rajasthan. The <2 μm fraction was purified by sedimentation and centrifugation. X-ray diffraction revealed that main constituent of this bentonite was montmorillonite. The suspension was then converted into chloride free Na- and H-saturated montmorillonites by Aldrich and Buchanan's method[6]. Ca-saturated montmorillonite was prepared from the sodium form by an ion exchange technique. The concentration of the suspensions ranged from 15.0 to 16.5 g l^{-1}. The cation exchange capacity (CEC) as determined by Ganguli's method[7] was 72 meq per 100 g clay.

To study the effect of time, 10 ml of the clay suspension in their H-, Na- and Ca- forms were taken in several glass stoppered tubes and treated with 3, 5, 7 and 15 ml of 0.015 *M* $NiCl_2$ at 30°. Further one set with 15 ml of nickel chloride and 10 ml of H-, Na- and Ca- montmorillonites was also treated at 60°. The volume of the mixtures was made up to 25 ml with distilled water, the samples were then shaken for various periods ranging between 1/4 to 6 hours, then centrifuged and nickel estimated in the supernatant solution measured by EDTA titration using PAN as indicator. The extent of adsorption was estimated by the difference between the amount of nickel added and remaining in the supernatants. The results are given in Fig. 1.

The effect of the equilibrium *p*H on experiment was investigated at different *p*H values ranging from 2 to 10. Different *p*H values are obtained by adding 0.1 *N* HCl or 0.1*N* NaOH as required. 10 ml of appropriate clay suspension and 1, 2, 5 and 15 ml of 0.015*M* nickel chloride were shaken in several glass stoppered tubes. After making the volume 25 ml with distilled water the tubes were shaken for 3 hours, centrifuged and the nickel adsorbed calculated as above.

Experiments for a study of adsorption isotherms were conducted at *p*H values of the unamended H-, Na- and Ca- montmorillonite suspensions by taking 10 ml suspension of appropriate clay in a

* Author for correspondence.

large number of glass stoppered tubes, adding various concentrations of 0.015*M* nickel chloride, adjusting the mixtures to 25 ml with distilled water and shaking the tubes at 30° in the first set of experiments and 60° in the second set for 3 hrs in each case. The suspensions were then centrifuged and the residual nickel estimated with standard EDTA solution using PAN as indicator. The difference gave the amount of nickel adsorbed. A plot of the adsorption isotherms is given in Fig. 3.

The results of desorption of nickel from complexed montmorillonites with 0.1*N* NaCl, 0.1*M* KCl and 0.05 *M* $BaCl_2$ with a shaking time of 6 hrs are given in Table 2.

All the experiments were done in duplicate with suitable blanks.

Results and Discussion

The amount of nickel adsorbed as a function of time is plotted in Fig. 1 for different concentrations

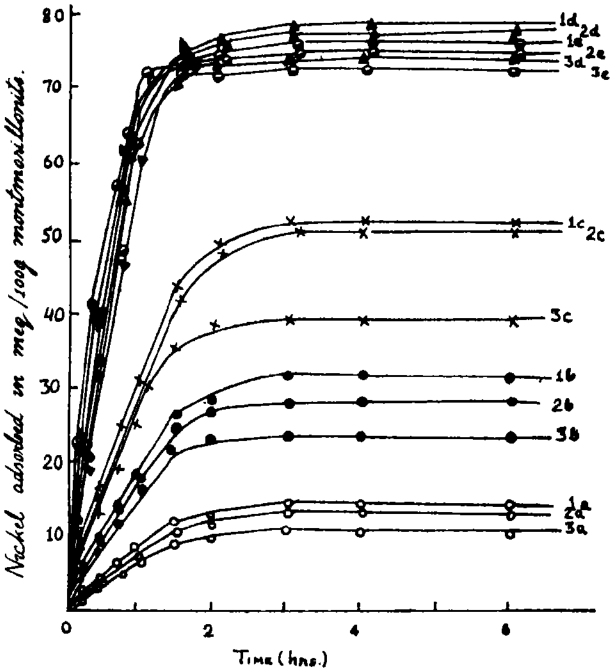


Fig. 1(a). Effect of time on the adsorption of nickel by H-montmorillonite are 30° and 60°. Concentration of nickel in meq per 100 g clay for curve 1 = (0.0, for curve 2 = 100 0, for curve 3 = 140.0 and for curve 4 = 3(0 0 at 30° and curve 5 = 300.0 at 60°.

1(b). Effect of time on the adsorption of nickel by Na-montmorillonites at 30° and 60°. Concentration of nickel in meq per 100 g clay for curve 1 = 54.5, for curve 2 = (0.9, for curve 3 = 127.3 and for curve 4 = 272.7 at 30° and curve 5 = 272.7 at 60°.

1(c). Effect of time on the adsorption of nickel by Ca-montmorillonite at 30° and 60°. Concentration of nickel in meq per 100 g clay for curve 1 = 56.2, for curve 2 = 93.8, for curve 3 = 131.3 and for curve 4 = 281.3 at 30° and curve 5 = 281.3 at 60°.

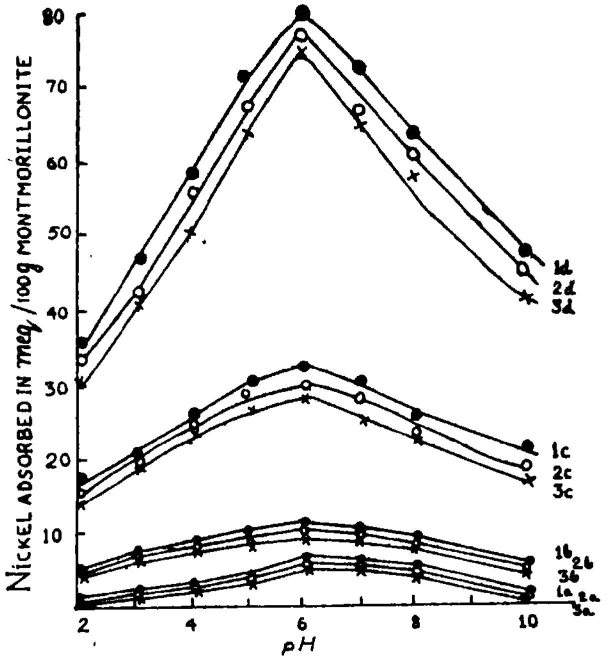


Fig. 2. Effect of *p*H on the adsorption of nickel by H(O)–, Na(●) and Ca(X) montmorillonites.

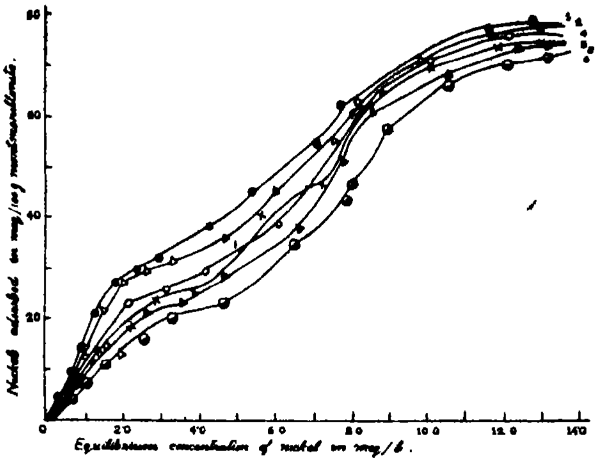


Fig. 3. Adsorption isotherms of H-, Na- and Ca- montmorillonites at ?0° and 60° 1, ● Na-mont. at 30°, 2. Δ. H- mont. at 30°, 3. × Ca- mont. at 30°, 4 O, Na mont. at 60° ; 5. ▲ H- mont. at 60° and 6 ◒ Ca – mont. at 60°.

of nickel chloride added to the H-, Na- and Ca-montmorillonite respectively. The system approaches equilibrium within 3 hrs, initially adsorption is rapid and then there is a slow increase. The initial rapid adsorption may be due to reversible exchange between nickel ions and the replaceable H-, Na- or Ca- ions of the clay surface. The slower increase in adsorption after 1½ hr was either due to slow penetration of Ni(II) ions to clay or due to chemical forces. Fig. 1 also indicates that the amount of nickel adsorption increases as the amount of nickel

TABLE 1—EFFECT OF TIME ON THE REACTION OF NICKEL WITH H-, Na- AND Ca-MONTMORILLONITES AT 30° AND 60°C

30°C

Time in minutes	H-montmorillonite			Na-montmorillonite			Ca-montmorillonite		
	Conc. of nickel in meq/100 g clay	k_1 min^{-1} $\times 10^3$	$t_{1/2} = \frac{0.693}{k_1}$ min^{-1}	Conc. of nickel in meq/100 g clay	k_1 min^{-1} $\times 10^3$	$t_{1/2} = \frac{0.693}{k_1}$ min^{-1}	Conc. of nickel in meq/100 g clay	k_1 min^{-1} $\times 10^3$	$t_{1/2} = \frac{0.693}{k_1}$ min^{-1}
15		2.26	307		2.87	242		2.16	321
30		2.36	293		2.87	242		2.14	324
45	60.0	2.30	301	54.5	2.74	253	56.2	2.17	319
60		2.32	300		2.79	248		2.15	322
90		2.30	301		2.76	251		2.19	317
100		1.43	485		1.72	403		1.21	572
15		3.18	218		3.78	183		2.90	239
30		3.18	218		3.76	184		2.93	237
45	100.0	3.25	213	90.9	3.80	182	93.8	2.90	239
60		3.24	214		3.89	180		2.90	239
90		3.21	216		3.85	181		2.93	237
100		2.04	339		2.30	301		1.58	432
15		3.82	181		4.50	154		3.52	197
30		3.80	182		4.48	155		3.48	199
45	140.0	3.84	180	127.3	4.60	150	131.3	3.48	199
60		3.87	179		4.53	153		3.52	197
90		3.86	179		4.58	151		3.50	198
180		2.53	274		2.92	237		1.97	352
15		4.22	164		4.96	140		3.99	174
30		4.24	163		4.93	141		4.00	173
45	300.0	4.28	162	272.7	4.98	140	281.3	4.04	172
60		4.28	162		4.90	142		4.04	172
90		3.16	216		3.51	198		3.23	214
180		1.66	417		1.89	361		1.69	410
Average value		3.64	214		4.19	187		3.50	219
60°C									
15		4.15	155		5.19	134		4.22	164
30		4.39	158		5.14	135		4.19	165
45	300.0	4.41	157	272.7	5.10	136	281.3	4.18	165
60		4.43	156		5.09	136		4.15	167
90		3.10	224		3.49	198		3.29	210
180		1.60	433		1.83	379		1.67	415
Average value		3.73	213		4.31	186		3.62	215

ions added to the aqueous suspension of clays increases, while with increase in temperature there is a decrease in the adsorption of nickel ions.

Applying the simple kinetic rate laws the order of reaction with respect to nickel was studied at different concentrations of nickel chloride and at fixed concentration of the H-, Na- and Ca- montmorillonites. The reaction followed the first order kinetics

$$K = \frac{2.303}{t} \log \frac{a_\infty}{a_\infty - X}$$

where K is rate constant, t time in sec., a_∞ amount of nickel adsorbed at equilibrium time and X amount adsorbed at time t. The results for different concentrations of nickel chloride so obtained are recorded in Table 1. The values of rate constants increased with increase in concentration of metal ion added, while the half life time decreased. This behaviour was characteristic of ion exchange process controlled by film and/or particle diffusion[8].

An examination of data vide Fig. 2 revealed that pH influenced the adsorption of nickel by montmorillonites. The adsorption increased upto a pH value 6.0 and thereafter it declines. In the case of highest range of concentration of exchangeable cation added the adsorption was in the neighbourhood of CEC of the clay at pH value 5.5, adsorption beyond CEC appeared may be due to fixation and precipitation reactions as occurred with lapse of time.

An examination of the adsorption isotherms in dilute suspensions in the equilibrium concentration range 0 to 14 meq of nickel ions per litre at 30° and 60° indicated that the isotherms were similar to class L as defined by Giles *et al*[9]. There are also some inflexions followed by a linear portion. The initial convex curvature in the isotherms indicate that nickel met no strong competition for adsorption sites from water. The change of slope in all the isotherms are indicative of the saturation of adsorptive sites in the substrate. The linear rise thereafter indicates slow penetration of solute molecules into

the micropores till they are filled up. With rise in temperature from 30° to 60° adsorption decreases, i.e. there is a weakening of the attractive forces between the nickel and montmorillonites, which is indicative of exothermic types of interaction. A greater amount of nickel is adsorbed by base saturated montmorillonites than the acid saturated montmorillonites. Adsorption followed the order Na- mont.>H- mont.>Ca- mont.

The desorption results (Table 2) indicate that upto 90% of nickel adsorbed on the acid and base saturated montmorillonites can be desorbed by NaCl, KCl or $BaCl_2$. Such a behaviour is indicative of a physical type of adsorption.

TABLE 2—DESORPTION OF NICKEL BY DIFFERENT ELECTROLYTES FROM THE SODIUM-, CALCIUM- AND HYDROGEN-ION SATURATED MONTMORILLONITE-NICKEL COMPLEXES

Form of montmorillonite	Nickel adsorbed (meq/100 g clay)	Nickel desorbed (meq/100 g clay) by		
		NaCl	KCl	$BaCl_2$
Hydrogen	71.8	63.1	63.8	64.8
Sodium	75.0	66.9	66.9	67.3
Calcium	72.1	64.0	64.8	64.9

The values of ΔE for adsorption of nickel on Na- and Ca-montmorillonites as determined by rate constants at 30° and 60° was found 10.2 to 10.6 k cal/mole respectively.

The relatively fast rate of adsorption, low values of activation energy and heat of activation (9.4 k cal) and desorption studies suggest that the adsorption of nickel on montmorillonites is of physical type[11], involving vander Waals forces and hydrophobic bonding between the nickel and clay surface in an aqueous system.

Acknowledgement

Thanks are due to Prof. S. S. Gupta, Principal, D. S. College, Aligarh for providing necessary facilities and encouragement so kindly rendered during the course of this work. The financial assistance given by U.G.C. to one of the authors (R.N.G.) is gratefully acknowledged.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1054-1055

Thermodynamic Study of Chelation of Rare Earth(III) Ions with 2,3-Dihydroxynaphthalene (DON)

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Manuscript received 12 December 1979, revised 29 July 1980, accepted 7 August 1980

The chelation of 2, 3-dihydroxynaphthalene with trivalent La, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y have been studied pH-metrically at 30°±0.5° in aqueous ethanol (10% v/v) at different ionic concentrations (0.05, 0.1, 0.15 and 0.2M KNO_3). Formation of 1 : 1 chelates are indicated. The order of stability is found to be

Ho > Dy > Tb > Y > Gd > Sm > Nd > Pr > La

The thermodynamic stability constants and free energies of chelation have been reported.

ALTHOUGH the complexes of 2, 3-dihydroxynaphthalene-6-sulphonic acid with rare earth(III) ions have been studied[1] potentiometrically, the literature for 2, 3-dihydroxynaphthalene complexes are scanty. Poluektov *et al*[2] have studied the stability of mixed ligand chelates of trivalent rare earths using DON as one of the ligands. In view of the above, our present work deals with the potentiometric study of chelation of trivalent La, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y with 2, 3-dihydroxynaphthalene at different ionic concentrations (0.05, 0.1, 0.15 and 0.2M KNO_3) in aqueous ethanol (10% v/v) at 30°±0.5° using Calvin-Bjerrum titration technique[3,4] as modified by Irving and Rossotti[5].

Experimental

The rare earth nitrates (Indian Rare Earth Ltd.) were dissolved in double distilled water and standardized by standard method[6]. All other reagents used were of AR grade and the solutions were prepared in boiled out doubly distilled water. Considering the low solubility of 2, 3-dihydroxynaphthalene in cold water under the experimental conditions, the solutions were prepared in aqueous ethanol (10% v/v).

A Philips pH-meter (PR 9405M) with glass and calomel electrodes was used for measuring the pH. The experimental details have been discussed in previous communications from this laboratory[7]. The titrations were performed in duplicates and the results found to be reproducible.

Results and Discussion

The formation functions $\bar{n}_A$, $\bar{n}$ and pL were calculated from the standard equations[5,8]. The observed pH meter readings were the same in water and aqueous ethanol mixture (10% v/v) for acid, ligand and metal titrations, thus eliminating the correction of the pH values. The proton-ligand stability constants were determined at different ionic concentrations (0.5, 0.1, 0.15 and 0.2M) and the values were computed by (1) interpolation at half $\bar{n}$ values, (2) pointwise calculation method, (3) correction term method[9] and (4) curve fitting method[10]. The mean values are given in Table 1.

TABLE 1—THERMODYNAMIC STABILITY CONSTANTS AND FREE ENERGIES OF CHELATION OF RARE EARTH(III) IONS WITH 2,3-DIHYDROXYNAPHTHALENE AT 30°C

Metal ions	Constants	μ=0.0M	μ=0.05M	μ=0.1M	μ=0.15M	μ=0.2M	$-\Delta G$ kJ mole^{-1}
H^+	log K_1^H	12.57	12.41	12.36	12.25	12.19	72.950
	log K_2^H	9.10	9.01	8.95	8.92	8.85	52.810
La^{3+}	log K_1	10.86	10.52	10.32	9.93	9.30	63.039
Pr^{3+}	log K_1	11.40	11.01	10.60	10.34	9.95	66.172
Nd^{3+}	log K_1	11.50	11.09	10.72	10.42	10.16	66.754
Sm^{3+}	log K_1	12.13	11.55	11.22	10.84	10.70	70.411
Gd^{3+}	log K_1	12.15	11.76	11.27	11.07	10.76	70.527
Tb^{3+}	log K_1	12.60	11.98	11.66	11.37	11.10	73.139
Dy^{3+}	log K_1	13.02	12.44	11.83	11.64	11.24	75.577
Ho^{3+}	log K_1	13.20	12.68	12.29	11.83	11.54	76.622
Y^{3+}	log K_1	12.25	11.78	11.54	11.21	10.98	71.107

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The metal ligand formation curves obtained by plotting $\bar{n}$ versus pL showed that the values of $\bar{n}$ vary between 0.1 and 0.9, thereby indicating the formation of only 1 : 1 complex in these systems. Above $\bar{n}\approx 0.9$, precipitation of the complexes starts, which disappears at pH$\approx$11. The pL values were computed by using the above computational techniques (except Correction Term method) and the mean values are tabulated in Table 1.

Thermodynamic stability constants were calculated by plotting log K_1 values against μ and extrapolating to zero ionic concentration. Log $K_1^{\mu=0}$ values were plotted against ionic radii (r^{-1})(Fig. 1). The stability increases with decrease in ionic radii, as expected, with a slight break at or near Gd^{3+} ion. The break near Gd^{3+} ion may be interpreted as corresponding to either the stability of half filled ($4f^7$) arrangement of Gd^{3+} ion or the changes in ionic radii[11] centering at the Gd^{3+} ion which allows a change in coordination number of the cations.

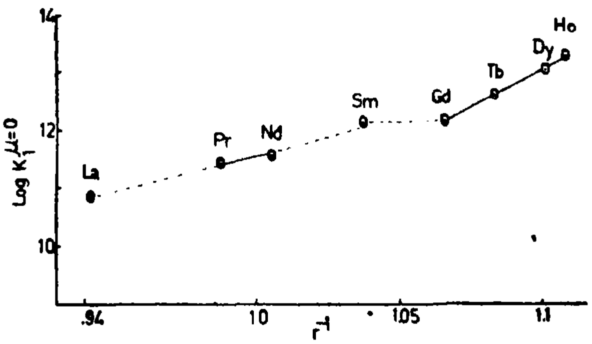


Fig. 1. Plot of Thermodynamic Stability Constants (log $K_1^{\mu=0}$) versus Ionic radii (r^{-1}).

The free energies of the chelation reactions are calculated from the relation

$$-\Delta G = RT\ln K^{\mu=0}$$

and are given in Table 1.

Acknowledgement

The authors are thankful to Dr. H.L. Bhatnagar, Head of the Chemistry Department, Kurukshetra University, Kurukshetra for providing laboratory facilities and one of them (BCB) is also thankful to the UGC for providing a fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1056-1058

Studies on Pollutants : Spectrophotometric Determination of Nitrite as "Azoxine Dye"

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Manuscript received 22 April 1980, accepted 7 August 1980

Ten new reagent systems for determination of nitrite in water have been studied. A new system for the determination of nitrite using diazotised aromatic amine with 8-hydroxyquinoline as a coupling reagent has been developed. Sulphanilamide was found to be most suited out of the ten amines tried for the determination of nitrite. The λ_{max} of the dye is 500 nm. The Beer's law is followed in the range of 4-30 μg of nitrite per 25 ml. The molar absorptivity and Sandell's sensitivity are 30×10^4 litre mole^{-1} cm^{-1} and 0.0015 μg cm^{-2} respectively. The optimum reaction conditions and other analytical parameters such as, Beer's law, sensitivity and interferences due to foreign species have been studied.

NITRITES occur in water due to bio-degradation of nitrates and organic matter. Their presence in water indicates pollution[1]. Several methods have been suggested for the determination of trace amounts of nitrites in water[2-9]. Most of the methods are based on Griess-Ilosvay diazo reaction[10,11]. These are continuously modified by changing the diazotising reagent as well as coupling reagent[3,4,12,13].

In the present paper 8-hydroxyquinoline proposed recently as a coupling agent[9] has been used for the determination of nitrites in water using ten different amines. The method is based on the diazotisation of aromatic amine by nitrites present in water in acidic medium and coupling the resultant diazonium chloride with 8-hydroxyquinoline in alkaline medium with subsequent measurement of the coloured azoxine dye[14] photometrically. The sulphanilamide and 8-hydroxyquinoline system was found to be the most suitable for nitrite determination. The coloured dye obtained is very stable. The reaction is very sensitive for nitrite determination. Hence, various experimental parameters are evaluated for this reagent system.

Experimental

Apparatus : All the spectrophotometric measurements were done at ECIL spectrophotometer model GS 865 and Carl Zeiss Spekol with 10 mm matched silica cells. *p*H measurements were made on Systronic *p*H meter model 323.

Reagents :

Standard sodium nitrite solution : A standard solution containing 20 μg of nitrite per ml was prepared in deionized water. A few drops of chloroform were added as stabilizer.

Diazotising reagent solution : 0.2% w/v solutions of recrystallized substituted anilines were prepared in 95% alcohol.

Coupling reagent 8-hydroxyquinoline solution : 0.2% w/v solution in 95% alcohol was prepared.

Sodium hydroxide solution : 2*N* solution was prepared in glass distilled water.

EDTA solution : 10% w/v solution was prepared in water. All the chemicals used were of analytical reagent grade.

Procedure :

An aliquot of water sample containing nitrite (4-30 μg) was taken in 25 ml volumetric flask. To this was added 1 ml of diazotising reagent and appropriate acidity was obtained by adding dilute hydrochloric acid (0.1*N*). The contents were shaken for 5 minutes (for *p*-anisidine 40-50 minutes are required). Then 1 ml of 8-hydroxyquinoline and 1 ml of EDTA were added and the contents were made alkaline with 3 ml of 2*N* sodium hydroxide for colour development. The volume was made up to the mark with glass distilled water. The *p*H of the solution was ~11. The absorbance of the coloured dye was measured against the reagent blank at appropriate wavelength.

Results and Discussion

The azoxine dyes formed by coupling the different diazotised aromatic amines with 8-hydroxyquinoline are colourless in the acidic medium while intensely coloured in alkaline medium. The diazotisation reaction is dependent on acidity. It was also found that with *p*-anisidine the colour development is slow.

The coupling of the diazotised amine takes place below 30° at 5 position out of the two possible positions[15] (i.e., at 5 and 7).

Absorption spectra, acidity and molar absorptivity :

The wavelength of maximum absorption against the reagent blanks for 'azoxine' dyes were determined by plotting the graph between wavelength and absorbance. The wavelengths of maximum absorption are given in Table 1.

TABLE 1—ACIDITY AND SPECTRAL CHARACTERISTICS

Sl. No.	Reagents	Acidity Range	λ_{max} nm	ϵ_{max} lit. $mol^{-1}cm^{-1}$
1.	Aniline	0.09 *N* and above	480	19×10^{3}
2.	Sulphanilic acid	0.01 *N* and above	500	29.5×10^{3}
3.	Sulphanilamide	0.05 *N* and above	500	30×10^{3}
4.	2-5 dimethoxy aniline	0.015 *N* – 0.05*N*	500-510	21×10^{3}
5.	*o*-nitroaniline	0.04 *N* – 0.08*N*	510	25×10^{3}
6.	*m*-nitroaniline	0.02 *N* and above	500	28.5×10^{3}
7.	*o*-anisidine	0.02 *N* – 0.06*N*	490	23×10^{3}
8.	*p*-anisidine	0.01 *N* and above	490	25.5×10^{3}
9.	3, 4 dimethyl aniline	0.03 *N* and above	480	20×10^{3}
10.	2, 6 dimethyl aniline	–	General absorption in visible region.	

The influence of acidity on diazotisation for obtaining maximum molar absorptivity was determined by varying acidities from 0-4*N* with dilute hydrochloric acid (0.1*N*) The acidity ranges for diazotisation and λ_{max} of the dyes for 20 μg of nitrite are given in Table 1.

It is apparent from Table 1 that substituent such as $-NO_2$, $-CH_3$ etc. when present in ortho position in the diazonium salt, the system is less sensitive. It may be due to steric hindrance or ortho effect. However, more studies in this direction will be useful.

The sulphanilamide was found to be the best out of 10 aromatic amines tried. Hence it was studied in detail.

Effect of Reagent :

It was found that at least 1 : 1 molar ratio of nitrite to sulphanilamide is necessary for complete diazotisation. To achieve the maximum colour development, at least 1 : 10 molar ratio of nitrite to 8-hydroxyquinoline is required. A large excess of both the reagents, can be tolerated without change in absorbance.

Stability and Composition of the dye :

The absorbance of the coloured system was found to be unchanged after keeping it for 3 days at varying temperatures from 20-40°. The composition of dye was determined by Job's method. The results interpreted from the curve plotted with $NO_2^-/(NO_2^-)$+(sulphanilamide), against absorbance and $NO_2^-/(NO_2^-)$+(8-hydroxyquinaline), against absorbance indicate that nitrite : sulphanilamide ratio is 1 : 1 and nitrite : 8-hydroxyquinoline ratio is 1 : 1.

Beer's law and Sandell's sensitivity :

The Beer's law is obeyed from 4-30 μg of nitrite

TABLE 2—EFFECT OF FOREIGN SPECIES IN THE DETERMINATION OF NITRITE (10 μg NO_2 in 25 ml)

	Species added	Amount added in ppm	Absorbance		Species added	Amount added in ppm	Absorbance
	NH_4^+	30	0.261		Ni^{2+}	20t	0.261
	As^{3+}	40	0.265		Sn^{2+}	20	0.262
*a	Al^{3+}	40t	0.265		WO_4^{2-}	60t	0.262
*a	Ba^{2+}	240t	0.262		PO_4^{3-}	20	0.261
*b	Bi^{3+}	20t	0.262		CN^-	80	0.265
*a	Ca^{2+}	60t	0.265		I^-	20	0.26
*a	Co^{2+}	130t	0.260		SCN^-	80	0.261
*a	Cr^{3+}	0.8t	0.261		NO_3^-	40	0.262
	Cu^{2+}	0.2	0.263		CO_3^{2-}	50	0.262
*d	Cu^{2+}	16.0	0.260	*c	SO_2	4	0.260
*a	Hg^{2+}	150t	0.260		Aniline	5	0.260
*a	Pb^{2+}	40	0.260		Benzene	10	0.263
	MoO_4^{2-}	20	0.260		Formaldehyde	100	0.265
*a	Mg^{2+}	40	0.260		Phenol	80	0.261
*b	Fe^{3+}	0.4	0.260				
	Fe^{2+}	0.004	0.220				

Note :

*a In presence of 1 ml of 10% EDTA.

*b In presence of 1 ml of 10% Sodium Potassium Tartrate.

*c In presence of 0.5 ml of 1% H_2O_2 (20 volume) H_2O_2.

*d In presence of 1 ml of 1% KCN.

*t Tolerance limit.

per 25 ml at 500 nm. The optimal concentration range evaluated from a Ringbom curve[16] is 7-26 μg nitrite/25 ml. The Sandell's sensitivity is 0.0015 μg cm^{-2} at 500 nm.

Effect of foreign species :

To evaluate the analytical potentiality of the reagent, the interferences due to different species present in water were studied. The foreign species were added in known amounts to nitrite solution (10 μg) before diazotisation and the absorbance was measured after developing the colour as described in general procedure. The data is presented in Table 2. The interferences of certain ions were corrected by adding EDTA (marked with *a), sodium potassium tartrate (marked with *b), hydrogen peroxide (marked *c) and potassium cynide (marked *d).

When all the ions excluding Cu^{2+} and KCN are added simultaneously to nitrite solution, the turbidity is obtained making determination unreliable. A synthetic sample containing 20 ppm of Mg^{2+}, Pb^{2+}, Ca^{2+}, Ba^{2+}, Cl^-, SO_4^{2-}, NO_3^- in tap water caused no interferences in the determination of nitrite.

Precision and reproducibility :

The precision of the method is high. The standard deviation and relative standard deviation were found to be ± 0.06 and ± 0.6 respectively.

The above method is suitable for determining trace amount of nitrites in water. The proposed method has following advantages over the α-napthylamine method, which is widely accepted as standard method for determination of nitrite.

1. It requires less time for analysis.
2. The stability of the reagent and the dye is higher.
3. It is free from rigorous control of pH and temperature.

Note : The present system has been found to be suitable for the determination of nitrogen dioxide in air. The collection efficiency of the alkaline 8-dydroxyquinoline reagent is found to be around 95% and NO_2/NO_2^- factor is found to be 0.75 which is in good agreement with the finding of Nash[17] (0.74).

The nitrogen dioxide is absorbed in 8-hydroxyquinoline. In this system nitrogen dioxide was converted to nitrite which was then used to diazotise the acidified amine and the colour was developed as described in procedure[18].

Acknowledgement

We wish to thank Dr. S. G. Tandon, for providing facility. One of us (A.B.) is thankful to University Grants Commission, New Delhi, for the award of a Junior Research Fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1059-1061

Spectrophotometric Method for the Determination of Cobalt

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Manuscript received 25 January 1977, revised 11 October 1977, accepted 26 July 1980

Spectrophotometric method for the determination of cobalt is given. The basis of the method is to convert cobalt into the stable and less sensitive to light trismalonato-cobaltate(III) anion. Iron, nickel and chromium may be present in a reasonable amount. The accuracy of the method is better than 2% of the quantity estimated.

COBALT reacts with so many ligands with the formation of coloured cobalt complexes. These coloured cobalt complexes have been used extensively for the detection and estimation of cobalt. Among these are the Carbonate CO_3^{2-} and Oxalate $C_2O_4^{2-}$. Telep and Boltz[1] have shown that the triscarbonatocobalt(III) has an absorbancy maximum in ultraviolet region at 260 mμ. The green colour of triscarbonatocobaltate(III) complex is specific for cobalt and has been used as basis for colorimetric method for cobalt determination[2,3]. The same complex was also utilized as a basis for titrimetric method for analysis of cobalt complexes[4,5]. An iodometric method for the determination of cobalt based on the conversion of cobalt to triscarbonatocobaltate(III) complex has been given by Laitinen and Burdett[6]. A polarographic method for the determination of cobalt as trisoxalatocobaltate(III) has been given by Kolthoff and Watters[7]. The green trisoxalatocobaltate(III) has a maximum absorption at 605 mμ, and spectrophotometric method for cobalt determination based on this complex was given by Cartledge and Nichols[8]. Reaction between Malonate $C_3H_2O_4^{2-}$ and Cr(III) has been used as photometric method for determination of chromium[9].

Herein a spectrophotometric method for cobalt determination based upon the formation of green trismalonatocobaltate(III) complex[10] is described. This complex has two absorption maxima at 425 mμ and 615 mμ with maximum extinction coefficients of 114 and 128 respectively. The method is based upon oxidizing cobaltous ion in weakly acidic solution of potassium malonate according to the reaction

$$2CoCl_2 + 7K_2C_3H_2O_4 + 4HC_2H_3O_2 + PbO_2 \longrightarrow 2K_3[Co(C_3H_2O_4)_3] + PbC_3H_2O_4 + 4KCl + 2H_2O + 4KC_2H_3O_2$$

Experimental

Unicam SP. 500 series 2 spectrophotometer with 1 cm, silica cells was used for the absorbancy measurements.

Standard cobalt solution was made by dissolving cobaltous chloride (A.R. Grade) in redistilled water and its cobalt content was determined by three successive electrolytic method. Potassium malonate solution was made from the neutralization of potassium hydroxide with malonic acid. Other solutions were prepared by dissolving their salts in water to get the required concentration.

Maximum Extinction Coefficient :

The maximum extinction coefficients of the cobalt(III) complex malonate at 425 mμ and 615 mμ were estimated. Solutions of reprecipitated potassium trismalonatocobaltate(III) were made and the absorbance was recorded. 1.0728 g (0.002 mol) of $K_3[Co(mal)_3]3H_2O$ was taken and dissolved and made up to 100 ml in a volumetric flask. This gave 0.02*M* solution. Another four solutions were made from 0.02*M* solution by dilution. All were made to 100 ml in volumetric flasks and the optical densities were measured at 425 mμ and 615 mμ. The slope of the curve obtained from plotting optical density against concentration gave the maximum extinction coefficient. Any small amount of cobaltous malonate resulting from slight decomposition of the complex has negligible effect since its extinction coefficient is 2.7.

The molar concentration of trismalonatocobaltate anion could be calculated as follows :

$$C = \frac{d}{El}$$

in which d is the measured density $\left(\log \frac{I_0}{I}\right)$, E is maximum extinction coefficient at defined wave

TABLE 1—DETERMINATION OF MAXIMUM EXTINCTION COEFFICIENT

Wave length in mμ	Molar Conc. of $K_3[Co(mal)_3]3H_2O$	Density
615	0.002	0.274
615	0.004	0.538
615	0.006	0.770
615	0.008	1.020
615	0.020	—

Maximum Extinction Coefficient is 128.4.

TABLE 2—DETERMINATION OF MAXIMUM EXTINCTION COEFFICIENT

Wave length in mμ	Molar Conc. of $K_3[Co(mal)_3]3H_2O$	Density
425	0.002	0.242
425	0.004	0.475
425	0.006	0.680
425	0.008	0.918
425	0.020	—

Maximum Extinction Coefficient is 114.

length and l is the cell length in cm. The cobalt content of the sample in mg can be estimated from the molar concentration C. If the oxidised solution was diluted to 100 ml before absorption measurements and assuming one cm cell was used, the weight of cobalt was determined from the relation :

$$\text{mg Co} = 45.9 \text{ d}$$

Spectrophotometric Determination of Cobalt :

A neutralized sample containing between 1 and 20 mg of cobalt in a volumetric flask was taken and 2 ml of glacial acetic acid, 5 ml of 20% ammonium acetate, 10 ml of 0.5*M* potassium malonate and 1 g of lead dioxide were added. The sample was kept for 10 to 20 minutes and shaken at every five minutes. The solution was then diluted without filtration to the mark. The flask was shaken twice and allowed to settle for few minutes and the solution was then filtered through a Whatman No. 42 filter paper. The first batch of the filtrate should not be taken ; the second batch was taken directly into the absorption cell and the optical density was measured.

Results

Interfering Elements :

Chromium(III), iron(III), nickel, copper and manganese interfere. Chromium(III) interferes but can be converted into weakly absorbing dichromate by preliminary oxidation. Iron(III) and nickel have a weak absorption at 615 mμ Tables (5a, 5b and 5c). Copper and manganese should be removed before oxidation of cobalt. The effects of the interfering elements were shown in terms of mg of cobalt. Even when comparatively large amount of the interfering elements are present only small fraction in mg is going to be added to the cobalt analysis result. Cobalt determination in the absence and presence of these interfering elements are shown in Tables 3 and 4.

TABLE 3—DETERMINATION OF COBALT

mg Co taken	Volume of Sol	Density	mg Co obt.	mg Error
1.91	100	0.042	1.91	+.000
3.82	100	0.082	3.75	−0.07
5.73	100	0.123	5.66	−0.07
9.55	100	0.212	9.74	+0.19
11.66	100	0.258	11.86	+0.20
13.37	100	0.294	13.52	+0.15
15.28	100	0.330	15.19	−0.09
17.19	100	0.375	17.23	+0.04
19.10	100	0.418	19.23	+0.13

TABLE 5a—INTERFERING ELEMENTS

mg of Ni	Volume of solution ml	Density	mg Co. represented
10	100	0.005	0.22
20	,,	0.007	0.32
30	,,	0.008	0.36
40	,,	0.009	0.41
50	,,	0.010	0.45
60	,,	0.011	0.50
70	,,	0.130	0.59

TABLE 5b

mg of Fe	Volume of solution ml	Density	mg Co. represented
10	100	0.001	0.04
20	,,	0.003	0.13
30	,,	0.004	0.18
40	,,	0.004	0.18
50	,,	0.005	0.22
60	,,	0.006	0.27
70	,,	0.007	0.32

TABLE 5c

mg of Chromium as $K_2Cr_2O_7$	Volume of solution ml	Density	mg Co. represented
10	100	0.004	0.18
20	,,	0.005	0.22
30	,,	0.006	0.27
40	,,	0.007	0.32
50	,,	0.008	0.36
60	,,	0.009	0.41
70	,,	0.010	0.45

TABLE 4—DETERMINATION OF COBALT IN THE PRESENCE OF INTERFERING ELEMENTS

mg of Co taken	mg of Ni added	mg of Cr as $K_2Cr_2O_7$ added	mg of Fe added	Volume of solution ml	Density	mg of Co obt	mg Error
8.55	9.6	5.17	36.18	100	0.193	8.86	+.31
11.40	11.2	6.03	42.21	,,	0.249	11.44	+.04
14.20	12.8	6.89	48.24	,,	0.317	14.57	+.37
17.10	14.4	7.76	54.27	,,	0.376	17.38	+.28
19.95	16.0	8.62	60.30	,,	0.439	20.18	+.23
22.80	17.6	9.48	66.33	,,	0.494	22.68	+.12

Comparison among carbonato, oxalato and malonato cobalt(III) complexes as methods for cobalt determination, carbonato complex is not stable and an excess of oxidising agent is required to maintain cobalt in the complex forms. The u.v. spectrum of the carbonatocobalt(III) complex is more sensitive than the visible spectrum[1]. On the other hand, the oxalato cobalt(III) complex is sensitive to light. Thus using the oxalato method the complex should not be exposed to bright light, The advantage of the malonato method lies in the fact that the trismalonatocobaltate(III) anion is stable in solution and not sensitive to light.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1062-1065

IR and Raman Spectra of Some Ferrocene Derivatives. Torsional Barriers and Thermodynamic Functions

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Manuscript received 3 June 1980, accepted 25 August 1980

The IR and Raman spectra of gaseous $(C_5H_5)Fe(C_5H_4COCH_3)$ and $(C_5H_4COCH_3)_2Fe$ were recorded in the frequency range 20 – 4000 cm^{-1}. Both the gaseous complexes show a Raman absorption at 41±2 cm^{-1} which was assigned to the torsional frequency $\tilde{\omega}_{0,1}$. In these molecules a barrier of 1000±100 cal/mol restricts the rotation of the cyclopentadienyl ring with respect to the rigid frame. The thermodynamic functions of the gaseous ferrocenes are reported in the temperature range 298 – 450K.

As part of our ongoing program concerned with the investigations of organometallic compounds, the IR and Raman spectra of the ferrocene derivatives $(C_5H_5)Fe(C_5H_4COCH_3)$ and $(C_5H_4COCH_3)_2Fe$ were carried out. The principal aim of our work was to calculate the rotational barriers of these molecules and to compare them with the value determined for ferrocene[1-3] and other metallocenes of transition metals[4-7]. It is in fact highly interesting from a spectroscopic point of view to understand the influence of the substitution of an atom or the addition of a group on the torsional barriers. Recent studies allowed the evaluation of the barriers of restricted rotation of solid and gaseous molecules as dicyclopentadienyl chloride of titanium, zirconium and hafnium[4,5], cyclopentadienyl chloride of titanium[5], cyclopentadienyl trihalides of germanium[6] and methyltitanium trihalides[7]. From these investigations it was concluded that no significant changes occur, in the limit of the experimental errors, in the height of the barriers when different halides are linked to the central atom as in the $(C_5H_5)MX_3$ systems (M = Ti, Ge ; X = Cl, Br, I) and when the C_5H_5 ring is bound to various metals as in the above mentioned complexes and in the $(C_5H_5)_2MCl_2$ molecules[4,5] (M = Ti, Zr, Hf). Therefore, it is interesting to study the behaviour of the rotational barriers of the ferrocenes considered in this work, being the substitution directly carried out, on the five-membered ring.

Experimental

The samples are commercial products (99.95% purity degree) supplied by Koch-Light Laboratories.

The IR spectra were recorded in the range 20-4000 cm^{-1} by using a Perkin-Elmer 180 IR grating spectrophotometer. The Raman spectra were run by a Cary Raman 81 spectrometer equipped with a He-Ne Laser as exciting source. Resistively heated stainless steel cells, 30 cm pathlength, were employed to record the spectra of the gaseous compounds. The cells were kept at 400 K during the spectroscopic measurements ; iron-constantan thermocouples were used at temperature monitors. The cells were filled with nitrogen at one atm. as a gas diffusion barrier and to avoid the condensation of the vapours on the optical windows. The IR and Raman spectra of the solid samples were recorded both at room and cryogenic temperatures (77 and 4.2 K) ; in the latter case a conventional cryostat working with liquid nitrogen and helium as cooling media was employed. High pressure Raman spectra were run in the gas phase at 5 atm. in order to reveal the torsional fundamentals. The IR and Raman frequencies are accurate in the gas phase within to ±2 cm^{-1} and ±1 cm^{-1} in the solid phase.

Results and Discussion

The IR and Raman spectra of the investigated compounds show the characteristic features of the ferrocenes derivatives[8,9] consisting of the appearance in the IR spectra of some of the g-type bands of ferrocene, otherwise only Raman active and of most of the A_{1u}, A_{2g} and E_{2u} modes inactive in the D_{5d} symmetry. The presence of the $COCH_3$ group, in fact, causes the lowering of the molecular symmetry of ferrocene from D_{5d} (staggered conformation) to the inferior symmetries. Accordingly the breakdown of the selection rules of the highest symmetry should be inevitable. Often the study of the spectra of metallocenes is made easy using the approximation of the local symmetry[9,10]. It must be pointed out, however, that the selection rules of the local symmetry are not always followed, so that IR or Raman modes can appear in both the spectra. According to this approximation, the cyclopentadienyl vibrations regarded under the C_{5v} local

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symmetry[4] are distributed as $3A_1+A_2+4E_1+6E_2$. As regards the substituted ring, although the single $C_5H_4COCH_3$ unit is nominally a C_s symmetry, its molecular symmetry is raised to C_{2v} if the $COCH_3$ group is considered freely rotating. Therefore, its fundamentals are distributed as $9A_1+3A_2+8B_1+4B_2$. The description of the ring vibrations is reported in Table 1 which also indicates their origin to the normal modes of the unsubstituted ring. The $\omega(7b)$, $\omega(9a)$ and $\omega(10b)$ vibrations are replaced by the out-of-plane and in-plane ring-$COCH_3$ bendings and ring-$COCH_3$ stretching respectively for the $C_5H_4COCH_3$ unit. The skeletal modes, which involve the metal atom motions, belong to the following symmetry species under the D_{5d} symmetry : $A_{1g}+A_{1u}+A_{2u}+E_{1g}+2E_{1u}$. These modes are described in Table 2 where the vibrations

TABLE 1—DESCRIPTION OF THE RING VIBRATIONS IN TERMS OF LOCAL SYMMETRIES

C_5H_5 (C_{5v})			$C_5H_4COCH_3$ C_{2v}			Vibration[a]
A_1	(IR, R)[b]	ω_1	A_1	(IR, R)	ω_1	νCH
		ω_2	B_2	(IR, R)	ω_2	γCH
		ω_3	A_1	(IR, R)	ω_3	breathing
A_2	(ia)[b]	ω_4	B_1	(IR, R)	ω_4	δCH
E_1	(IR, R)	ω_5	A_1	(IR, R)	ω_{5a}	νCH
			B_1	(IR, R)	ω_{5b}	
		ω_6	A_1	(IR, R)	ω_{6a}	δCH
			B_1	(IR, R)	ω_{6b}	
		ω_7	A_2	(R)	ω_{7a}	γCH
			B_2	(IR, R)	ω_{7b}	γ ring-$COCH_3$
		ω_8	A_1	(IR, R)	ω_{8a}	νCC
			B_1	(IR, R)	ω_{8b}	
E_2	(R)	ω_9	B_1	(IR, R)	ω_{9b}	νCH
			A_1	(IR, R)	ω_{9a}	ν ring-$COCH_3$
		ω_{10}	A_1	(IR, R)	ω_{10a}	δCH
			B_1	(IR, R)	ω_{10b}	δ ring-$COCH_3$
		ω_{11}	A_2	(R)	ω_{11a}	γ CH
			B_2	(IR, R)	ω_{11b}	
		ω_{12}	A_1	(IR, R)	ω_{12a}	νCC
			B_1	(IR, R)	ω_{12b}	
		ω_{13}	A_1	(IR, R)	ω_{13a}	δCC
			B_1	(IR, R)	ω_{13b}	
		ω_{14}	A_2	(R)	ω_{14a}	γCC
			B_2	(IR, R)	ω_{14b}	

(a) ν=stretching, δ=in-plane deformation, γ=out-of-plane deformation.

(b) IR=infrared active, R=Raman active, ia=inactive.

TABLE 2—DESCRIPTION OF THE SKELETAL AND METHYL VIBRATIONS

Ring-Fe-Ring (D_5d)	Vibration[a]
A_{1g} (R)	ν_s Fe-Ring
A_{1u} (ia)	torsional mode
A_{2u} (IR)	ν_a Fe-Ring
E_{1g} (R)	Ring tilt
E_{1u} (IR)	δ Ring-Fe-Ring
E_{1u} (IR)	Ring tilt
CH_3 internal modes (C_{3v})	
A_1 (IR, R)	ν_s CH
	δ_s CH_3
E (IR, R)	ν_a CH
	δ_a CH_3
A_2 (ia)	ρ CH_3

(a) The further vibrations are: νCO, $\nu COCH_3$, δCO, γCO, δCH_3, γCH_3 ; s=symmetric, a=antisymmetric, ρ=rocking.

TABLE 3—ASSIGNMENT OF THE OBSERVED IR AND RAMAN BANDS

C_5H_5 IR (cm⁻¹)	ring vibrations R (cm⁻¹)	$C_5H_4COCH_3$ IR (cm⁻¹)	ring vibrations R (cm⁻¹)	Assignment[a]
3110	3110	3110	3110	ω_1
807	806	777	777	ω_2
1112	1110	1045	1044	ω_3
1255[b]	1255[b]	1260[b]	1260[b]	ω_4
3085	3085	3120	3120	ω_{5a}
		3090	3090	ω_{5b}
1015	1015	1050	1050	ω_{6a}
		980	982	ω_{6b}
825	824	788	820	ω_{7a}
			290	ω_{7b}
1425	1426	1445	1444	ω_{8a}
		1410	1410	ω_{8b}
	3055	3070	3068	ω_{9b}
		1000	1001	ω_{9a}
	1170	222	221	ω_{10a}
		205	204	ω_{10b}
	1071		1019	ω_{11a}
		987	989	ω_{11b}
	1555	1620	1620	ω_{12a}
		1583	1585	ω_{12b}
	897	850	852	ω_{13a}
		887	888	ω_{13b}
	556		567	ω_{14a}
		320	322	ω_{14b}
300	300	298	298	ν_s Fe-Ring
	41[c]		41[c]	torsion
475	475	470	471	ν_a Fe-Ring
380	378	371	370	
165	166	145	145	Ring tilt
490	490	311	310	
		CH_3 internal modes		
2911	2911	2907	2906	ν_sCH
2940	2942	2935	2933	ν_aCH
2965	2964	2955	2955	
1380	1378	1377	1377	$\delta_s CH_3$
1470	1469	1466	1465	$\delta_a CH_3$
1460	1457	1455	1456	
1025	1023	1018	1016	ρCH_3
		$COCH_3$ vibrations		
1698	1698	1687	1688	νCO
1677	1677	1679	1678	
1222	1222	1220	1220	$\nu COCH_3$
650	649	645	646	δCO
715	717	718	716	
510	511	509	509	γCO
350	350	355	356	
666	666	666	665	δCH_3
520	520	520	520	γCH_3

(a) See Tables 1 and 2.

(b) Observed in the IR and Raman spectra at high pressure or at Low temperatures (see text).

(c) Observed in the Raman spectra at high pressures or at low temperatures (see text).

related to the ring-$COCH_3$ group are also summarized. The assignment of the IR and Raman bands observed in the gas phase spectra is reported in Table 3; it was performed by comparing the present results with the previous ones reported for similar complexes[3,6-12]. The IR and Raman frequencies corresponding to the C_5H_5 and $C_5H_4COCH_3$ ring vibrations were found to be coincident, in the limit of the experimental errors, for both the compounds, so that they are not referred in Table 3 to a particular complex.

The spectroscopic expectations based on the approximation of the local symmetries are fulfilled in case of the ring vibrations. The skeletal modes do not follow the selection rules of the D_{5d} symmetry group displaying both IR and Raman activity. Particularly interesting is the discussion of the assignment of the CH in-plane deformation and of the torsional mode. The former vibration should be inactive according to the selection rules of the C_{5v} local symmetry of the five-membered ring while it is expected IR and Raman active in case of the substituted ring (see Table 1). The position of this band in the vibrational spectrum of ferrocene was established by normal coordinate calculations[18] at 1200 cm^{-1}. This band was observed at 1256 cm^{-1} in the IR spectrum ferrocene at low temperature[3] and its appearance would arise from a second order phase transition. It is also present in the IR and Raman spectra of other cyclopentadienyls[4-6] at cryogenic temperatures and in the gas phase at high pressures[5,6]. The spectra of the two complexes show no absorption in this region; this fact is surprising since one substituted ring is at least present in each molecule. This behaviour most probably seems due to the weakness of this vibration in the gas phase. However, working at high pressure (nitrogen at 5 atm) and at low temperature (77 and 4.2 K) in the gas and solid phases respectively, we were able to reveal this absorption in the IR and Raman spectra of both the ferrocenes at ca. 1260 cm^{-1}.

The internal rotation mode for these complexes is expected in the low region, not very far from the corresponding ferrocene frequency[3]. Our spectra do not indicate the presence of bands in the far IR and Raman. The torsional overtones have revealed a powerful mean[6,7,14] to evaluate the torsional fundamental $\bar{\omega}_{0,1}$. The Raman spectra recorded in the gas phase show absorptions at 81, 75 and 69 cm^{-1} (see Fig. 1) which could be assigned to the $\bar{\omega}_{0,2}$, $\bar{\omega}_{1,3}$ and $\bar{\omega}_{2,4}$ overtones respectively. If this assignment is correct, the following set of equations:

$$\bar{\omega}_{0,2} = 2\bar{\omega}_e(1-3x_e)$$
$$\bar{\omega}_{1,3} = 2\bar{\omega}_e(1-5x_e)$$
$$\bar{\omega}_{2,4} = 2\bar{\omega}_e(1-7x_e)$$

will provide the $\bar{\omega}_e$ and x_e values and through the equation

$$\bar{\omega}_{0,1} = \bar{\omega}_e(1-2x_e)$$

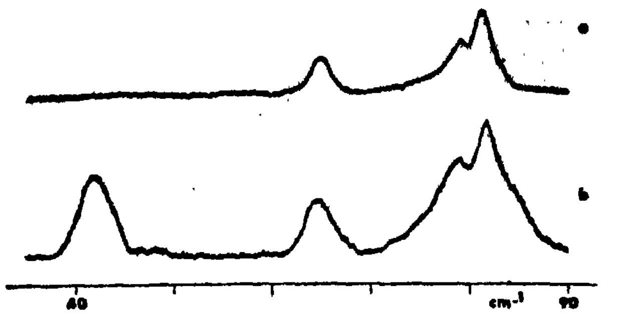


Fig. 1. Raman spectra of gaseous $(C_5H_5)Fe(C_5H_4COOCH_3)$ in the range 20-100 cm^{-1}: (a) 1.0 atm of N_2, (b) 5.0 atm of N_2.

the torsional fundamental $\bar{\omega}_{0,1}$ is evaluable. Our calculations yield as $\bar{\omega}_{0,1}$ the frequency at 42 cm^{-1}. In order to check this conclusion, we recorded the Raman spectra of the ferrocenes at different pressures of nitrogen (up to 5 atm). High pressure Raman spectroscopy was already employed to reveal the torsional fundamentals[6,7,14]. Under these conditions we observed a Raman band at 41 ± 2 cm^{-1} for both the complexes (see Fig. 1) supporting the correctness of our assignment. A further test was carried out recording the Raman spectra of the solid samples at cryogenic temperatures (77 and 4.2 K). Previous studies[5-7,14] indicate that internal rotation frequencies can also be detected in the solid phase at low temperatures. In this case a band at 42 ± 1 cm^{-1} was revealed for the investigated species. Similar experiments were performed in the far IR but with no success; it is in fact well known that these vibrations occur with negligible dipole moment changes so that the intensity of the IR bands are very feable[14].

Rotational barriers and thermodynamic functions:

The barriers of hindered rotation were calculated employing the equation[14]:

$$V(\text{erg}) = \frac{8\pi^2 c^2 \bar{\omega}_{0,1}^2 \, I(r)}{n^2}$$

where $\bar{\omega}_{0,1}$ is the experimental torsional fundamental, I(r) the reduced moment of inertia and n the order of the five-fold barrier. For both the complexes a barrier of 1000 ± 100 cal/mol was found; the associated uncertainty was estimated taking into account an error of ± 2 cm^{-1} in the frequency measurements due to the broadness of the Raman absorption and the evaluation of the reduced moment of inertia. It was calculated for each molecule employing the same structural parameters of ferrocene[3] while the bond lengths and angles of the $COCH_3$ group were assumed as the sum of the covalent radii of the linked atoms and equal to 120° respectively; the HCH angles of the methyl were considered tetrahedral.

The thermodynamic functions of the gaseous complexes were calculated using the standard

method of statistic thermodynamics[15]. The requested contributions to the partition function were evaluated employing the structural parameters assumed as already reported in the text and the vibrational frequencies summarized in Table 3. Only the electronic ground state was considered in these calculations and it was kept as a singlet $^1\Sigma$. The corrections for the internal rotation contribution were carried out according to the Pitzer treatment[16] on the ground of the calculated barrier $V = 1000 \pm 100$ cal/mol. The thermodynamic functions are listed in Table 4. The associated errors reported there are based on the uncertainty of ± 2 cm^{-1} in the frequency values and on the estimation of the molecular parameters.

TABLE 4—THERMODYNAMIC FUNCTIONS OF THE GASEOUS FERROCENE DERIVATIVES

T (K)	S°_T (e. u.)[a]	$-(G^\circ_T - H^\circ_0)/T$ (e. u.)[a]	$(H^\circ_T - H^\circ_0)$ (cal/mol)	S°_T (e. u.)[a]	$-(G^\circ_T - H^\circ_0)/T$ (e. u.)[a]	$(H^\circ_T - H^\circ_0)$ (cal/mol)
	$(C_5H_5)Fe(C_5H_4COOCH_3)$			$(C_5H_4COOCH_3)_2Fe$		
298.15	95.08	70.76	7252	96.52	71.95	7324
300	95.43	70.90	7361	96.87	72.09	7432
325	99.89	72.91	8769	101.33	74.10	8848
350	103.83	74.91_8	10122	105.27	76.11	10206
375	107.33	76.92	11406	108.77	78.11_8	11496
400	110.45	78.93	12607	111.89	80.12	12706
425	113.22	80.94	13721	114.66	82.13_8	13823
450	115.70	82.94_5	14739	117.14	84.14	14850
	± 0.25	± 0.25	± 10	± 0.25	± 0.25	± 10

[a] e. u. = cal/mol K.

Conclusions :

The rotational barriers of the ferrocenes considered in this study are quite close to the value derived for ferrocene[1,3]. In the light of these results we are led to conclude that the presence of one or two $COCH_3$ groups bound to the five-membered ring do not considerably alter the height of the torsional barrier of ferrocene. The conviction that these barriers almost exclusively depend on the nature of the metal-ligand bond is strengthened by the comparison between the present results and the previous ones[4-7]. For this purpose, the rotational barriers determined by spectroscopic data for a series of systems have been reported in Table 5. As a further development of our research program, we believe it would be interesting to verify the influence on the rotational barriers of strongly electronegative substituents or large size groups directly linked to one or both the cyclopentadienyl rings.

TABLE 5—SUMMARY OF THE TORSIONAL BARRIERS DERIVED FROM SPECTROSCOPIC DATA

Compound	V(cal/mol)	References
$(C_5H_5)_2Fe$	900 ± 300	1-4
$(C_5H_5)Fe(C_5H_4COOCH_3)$	1000 ± 100	this work
$(C_5H_4COOCH_3)_2Fe$	1000 ± 100	this work
$(C_5H_5)_2TiCl_2$	970 ± 100	4, 5
$(C_5H_5)_2ZrCl_2$	930 ± 100	4, 5
$(C_5H_5)TiCl_3$	380 ± 30	5
$(C_5H_5)GeCl_3$	390 ± 30	6
$(C_5H_5)GeBr_3$	370 ± 30	6
$(C_5H_5)GeI_3$	370 ± 30	6
$(CH_3)TiCl_3$	1500 ± 100	7
$(CH_3)TiBr_3$	1400 ± 100	7
$(CH_3)TiI_3$	1350 ± 100	7

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1066-1070

Conductometric and Spectrometric Studies on the Complexes of Ag(I) and Hg(II) with 1-Phenyltetrazoline-5-Thione

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Manuscript received 4 February 1980, revised 3 June 1980, accepted 27 August 1980

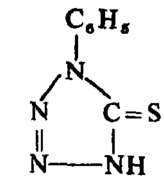
Ag(I) and Hg(II)-form stable complexes with 1-phenyltetrazoline-5-thione (1PT5TH). Their complexation has been studied in solution by conductometric titration method and the solid complexes formed were separated, analysed and their structures have been suggested on the basis of infrared spectroscopic and conductometric methods. The experimental results indicate that both the ions form 1 : 1 polymeric complexes having formula $[Ag(1PT5T)H_2O]_n$ and $[Hg(1PT5T)Cl.H_2O]_x$ where n may be larger than x. The coordination number of Ag(I) ion and that of Hg(II) ion is 4. Both the complexes are bonded to the central metal ions both through nitrogen as well as sulphur. Simultaneous bonding through S – and N – has resulted in the considerable decrease in the intensity of the νNH band, disappearance of thioamide band I, splitting of the thioamide band II, reduction in intensity of thioamide band III and disappearance of thioamide band IV, on complexation.

COMPOUNDS containing a thioamide moiety $H-\overset{|}{N}-\overset{|}{C}=S$ have been studied by several workers and it has been suggested that all such compounds give rise to four thioamide bands[1-4] in their IR spectra. They are all mixed bands and have contributions from δN – H, νC=N, νC=S and δC – H. The bond order higher than one for C=N and less than two for C=S arise because of the following equilibrium :

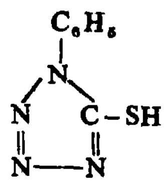
$$H-\overset{|}{N}-\overset{|}{C}=S \rightleftharpoons -N=\overset{|}{C}-S-H$$

The four thioamide bands appear around 1550 (band I), 1250 (band II), 900 – 1050 (band III) and 750 – 850 cm^{-1} (band IV) and these have contributions from (δN – H + δC – H), (δN – H + δC – H + νC=N), (νC=N + νC=S) and νC=S respectively.

It has been reported that for monodentate sulphur ligands (such as thiocyanate ion), band IV (νC=S) may be used as diagnostic of metal ligand bonding[5-22]. Metal-sulphur bonding results in red shift of about 50 cm^{-1} in the thioamide band IV and metal nitrogen bonding generally results in either no shift or blue shift of the order of 30-40 cm^{-1} in this band. A red shift of the order of about 100 cm^{-1} in the thioamide band IV is an indication of a bridging system[23-25]. 1-Phenyltetrazoline-5-thione contains one imino group, one thiocarbonyl group and three other nitrogen atoms for coordination. Hence it can act as a monodentate or bidentate ligand. It exists as a thione form (Fig. Ia) and also in thiol form (Fig. Ib) in solution[26].

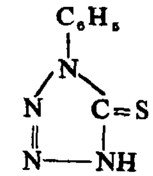


Thione form
(Fig. Ia)

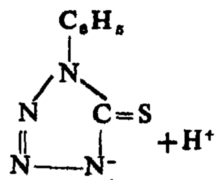


Thiol form
(Fig. Ib)

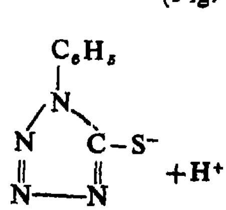
However, the IR spectra of 1-phenyltetrazoline-5-thione (1PT5TH) does not show the S – H peak in the region of 2500 cm^{-1}. The UV and visible spectra of the ligand also indicate the presence of a νC=S group in 1-phenyltetrazoline-5-thione. Lieber *et al*[27] have shown that thiocarbonyl group of 1-phenyltetrazoline-5-thione is electron withdrawing and the hydrogen linked with nitrogen atom at the four position of the heterocyclic ring is acidic.



(Fig. IIa)



(Fig. IIb)



(Fig. IIc)

The present work deals with conductometric studies and complexing behaviour of Ag(I) and Hg(II) ions with 1-phenyltetrazoline-5-thione. It also deals with the separation of the complexes and their characterisation by spectroscopy and magnetic moment measurement. The nature of shifts in the thioamide bands corresponding to nature of metal-ligand bonding has also been examined herein.

Experimental

All chemicals used in this work were of AnalaR quality.

Method for Preparation of Ligand and Complexes :

1-Phenyltetrazoline-5-thione :

Phenylisothiocyanate was prepared by method given in the literature[22] and 1-phenyltetrazoline-5-thione was prepared by the method of Lieber *et al*[23]. The ligand was recrystallised from ethanol. The molecular formula of 1-phenyltetrazoline-5-thione (1PT5TH) is $C_7H_6N_4S$ (molecular weight = 178). The analytical results of the ligand are given below :

Found : C, 46.88 ; H, 3.35 ; N, 30.45%
Calcd : C, 47.03 ; H. 3.39 ; N, 31.25%

1-Phenyltetrazoline-5-thionato aquo silver(I) polymer :

$[Ag(1PT5T)H_2O]_n$:

Silver nitrate and 1PT5TH were dissolved separately in ethanol and mixed in 1 : 2 molar ratio which formed immediate precipitate of the white complex. The complex was digested on water bath for about 30 minutes and filtered. It was washed with ethanol followed by ether and dried in an oven at 110°. The analytical results of this complex are given below :

Found : N, 18.90 ; Ag, 35.00%
Calcd. : N, 18.48 ; Ag, 35.65%

Aquochloro 1-phenyltetrazoline-5-thionato mercury (II) :

$HgCl(1PT5T)H_2O$:

Mercuric chloride and 1PT5TH were dissolved separately in ethanol and mixed in 1 : 2 molar ratio which formed immediate precipitation of the white complex. The complex was digested on water bath for about 30 minutes and filtered. It was washed with ethanol followed by ether and dried in an oven at 110°. Its analytical data are given below :

Found : N, 13.66 ; Hg, 46.14 ; Cl, 8.13%
Calcd. : N, 13.02 ; Hg, 46.52 ; Cl, 8.24%

Magnetic Measurement :

The magnetic measurement was done by Guoy balance at room temperature. These complexes were found to be diamagnetic.

Infrared Spectra :

The infrared spectra of the ligand and the complexes were recorded in KBr pellets using Perkin-Elmer model 621 infrared spectrophotometer in the range of 4000 to 200 cm^{-1}.

Conductometric Titrations :

Conductometric titrations were carried out by means of Sistronic conductometer model 302.

Results and Discussion

The analytical results of the Ag(I) complex indicate that its stoichiometry is $Ag(1PT5T)H_2O$ and that of the mercury(II) complex is $HgCl(1PT5T)H_2O$.

The conductometric titration of the ligand with the metal ions Ag(I) and Hg(II) was conducted as discussed below :

The following stock of solutions were prepared :

(a) 50 cc (0.005*M*) solution of ligand in aqueous ethanol.

50 cc (0.01*M*) $AgNO_3$ solution in aqueous ethanol.

(b) 50 cc (0.005*M*) solution of ligand in ethanol.

50 cc (0.01 *M*) solution of $HgCl_2$ in ethanol.

10 cc of the ligand solution (0.005 *M*) in aqueous ethanol was taken in the conductivity cell and 1 cc of the $AgNO_3$ solution was added each time and the conductivity recorded.

The results in case of Ag(I) complex show an increase in conductivity from 0.55×10^3 in Mohs cm^2 to 0.70×10^3 Mohs cm^2. The inflexion point at 5 ml is indicative of 1 : 1 complex having been formed and this agrees well with the composition of the solid complex.

In case of Hg(II) complex the conductivity measurements also show an inflexion at 5 ml indicative of a 1 : 1 complex.

Infrared Spectra :

The infrared spectral bands of the ligand and the complexes are given in Table 1.

TABLE 1—INFRARED BANDS OF THE LIGAND AND COMPLEXES (cm^{-1})

(1PT5TH)	[Ag(1PT5T)-$(H_2O)]_n$	[HgCl(1PT5T)-$H_2O]_x$	Assignments
–	3560 bm 3480 sh	3440 bm	H_2O
3080 bs 2950 bw	3060 vw 2920 vw	3060 vw 2020 vw	$\nu N-H+\nu C-H$ in ligand but $\nu C-H$ in complexes
– 1597 s 1512 vs	1615 vs 1590 s –	1615 bw 1595 m –	δH_2O Thioamide band I
1490 vs 1457 m	1490 s 1455 m	1495 s 1455 vw	
1383 m 1351 s 1327 m	1400 s 1370 vs 1340 vw	1400 sh 1370 s 1340 s	
1305 w 1295 w	1310 m 1295 w	1310 w 1295 vw	
1280 s	1280 w 1270 m doublet	1270 vw	Thioamide band II
1210 s 1175 w	1230 s 1170 m	1230 m 1170 vw	
1100 m	1110 s 1100 s doublet	–	
1090 m 1070 m	1080 vw 1070 m	1085 vw 1060 w	
1045 vs	1040 m	1045 w	Thioamide band III
1018 vw	1015 s	1015 m	
1000 m 985 vs 908 m 823 vw	990 m 910 m 880 vw	985 vw 910 vw 795 w	
785 m	–	–	Thioamide band IV
763 vw 750 s	755 vs 715 m	750 s –	
673 s 659 s	693 s 693 s doublet	692 s 692 s doublet	
573 vs 510 m 450 s 415 s	562 m 500 w 430 mb	565 m 496 vw 467 m 460 m	
390 w 350 w	390 vw 334 sh	370 vw 332 vw	
337 w	300 w	–	
328 w 320 m 310 m 295 vw 292 vw 267 vw	 250 sh 240 vw 220 vw	 250 s 220 w	

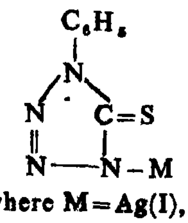
A comparison of the infrared spectral bands of the ligand and the complexes indicate that a lot of changes have occurred in infrared spectral bands of the ligand on complexation with Ag(I) and Hg(II) ions. Some of the important changes are described below :

(a) Two very broad and medium bands are observed at 3560 and 3480 cm^{-1} in the spectrum of the Ag(I) complex and one broad and medium band is observed at 3440 cm^{-1} in the spectrum of the Hg(II) complex. The spectrum of the ligand does not contain any band in this region. Thus, the presence of these bands indicate the presence of coordinated water in these two complexes. Coordinated water molecule has its νOH mode of vibration in this region[30-33].

(b) There is no infrared band in the 1600 cm^{-1} to 1700 cm^{-1} region in the spectrum of the ligand. But a very strong band is present at 1615 cm^{-1} in the spectrum of the Ag(I) complex and a weak broad band is present at 1615 cm^{-1} in the Hg(II) complex. These bands may be due to H_2O mode of the coordinated water in the complexes. The strong intensity of the 1615 cm^{-1} band in Ag(I) complex may be due to the polymeric nature of the Ag(I) complex, $[Ag(1PT5T)(H_2O)]_n$ and the low intensity of the 1615 cm^{-1} in Hg(II) complex, $[Hg(Cl)(1PT5T)H_2O]_x$ due to its less degree of polymerisation than in $[Ag(1PT5T)(H_2O)]_n$.

(c) *There is a new medium broad band at* 430 cm^{-1} in the spectrum of Ag(I) complex and a very weak absorption at this position in Hg(II) complex. They may be assigned to the liberational mode of coordinated water molecule as no such band is present in the spectrum of the ligand. This is also supported by the fact that liberational mode of coordinated water has been assigned in this region[34,35].

(d) There is a broad and strong band in the ligand at 3080 cm^{-1} which has been assigned to $\nu N-H$ and $\nu C-H$ modes of vibration. This band shifts to 3060 cm^{-1} in the Ag(I) and Hg(II) complexes with drastically reduced intensity. The reduction in intensity of this band on complexation is so large that only very weak band exists at 3060 cm^{-1} in the complexes. This may be taken as a proof for the replacement acidic hydrogen of the ligand by means of metal ion as shown below :



where M=Ag(I), Hg(II)

Fig. 3.

(e) **Normal coordinate analysis of organic compounds containing a thioamide group (H – N = C = S)** has been reported in the earlier literature. Agarwala and Rao[86] on the basis of normal coordinate analysis of ethylenethiourea molecule has suggested that the thioamide band I observed in the region of 1500 cm^{-1} is a mixed band having contributions from δNH(68 to 80%) and νCN (12 to 20%). The thioamide band II observed in the 1200 cm^{-1} region have contributions from νC=S (36%)+νCN (30%)+δNH (24%). The thioamide bands III observed in the region of 900-1050 cm^{-1} have main contributions from νC–C (24 to 34%)+νC=S (19 to 26%)+νCN (15-34%). The band IV observed in the region of 700 cm^{-1} possesses main contributions from νC=S (30%)+νCN (46%)+ring vibrational mode (11%). On the basis of the normal coordinate analysis of the tetrazole molecule and taking into consideration Agarwala and Rao[86] assignments of the thioamide bands, it seems reasonable to make the following assignments of the four thioamide bands of 1-phenyltetrazoline-5-thione[82] (Table 2).

TABLE 2—THIOAMIDE BANDS OF 1-PHENYLTETRAZOLINE-5-THIONE (cm^{-1})

Thioamide bands	I	II	III	IV
	1512 s	1280 s	1045 s	785 m
Assignments	(δNH+ νCN)	(νC=S+ νC–N+ δNH)	(νC–C+ νC=S+ νCN)	(νCS+νCN+ ring deformation)

(f) A comparison of the positions and intensities of the thioamide bands of the ligand and the complexes (Table 1) indicates that thioamide band I observed at 1512 cm^{-1} as a strong band in the infrared spectrum of the ligand disappears on complexation. Thus, there are two bands in the 1500-1600 cm^{-1} in the ligand but there is only one band in this region of the complexes. This may be taken as an additional proof of replacement of acidic hydrogen of NH group of the ligand by means of Ag(I) ion in Ag(I) complex and by Hg(II) ion in Hg(II) complex as shown in Fig. 3.

The thioamide band II observed as a strong band at 1280 cm^{-1} in the spectrum of the ligand gets split in the Ag(I) complex and the split bands are observed at 1280 cm^{-1} as a weak band and at 1270 cm^{-1} as a medium band. This band is observed at 1270 cm^{-1} in the spectrum of the Hg(II) complex as a very weak band. Slight lower shift and reduction in intensity of this band may be accounted for the coordination of the ligand to the metal ions through sulphur also. The reduction in intensity may be due to the fact that contribution of νC=S mode has been removed from this band due to the coordination of the ligand to the metal ions through sulphur. Similar explanation can be given for the reduction of intensity of the thioamide band III on complexation of the ligand with metal ions (Table 1).

The thioamide band IV is observed at 785 cm^{-1} as a medium band (Table 1). This band has almost disappeared from the spectra of the Ag(I) and Hg(II) complexes. As this band has major contribution from νC=S mode of vibration and also because coordination has taken place through sulphur also, this band as been shifted to lower frequency and has probably merged with the 755 cm^{-1} strong band of the Ag(I) complex and 750 cm^{-1} strong band of the Hg(II) complex.

The above discussion indicates that 1-phenyltetrazoline-5-thione is coordinated to the Ag(I) and Hg(II) ions through nitrogen as well as sulphur and water is coordinated to the metal ions. Thus, the following structures may be suggested to these complexes :

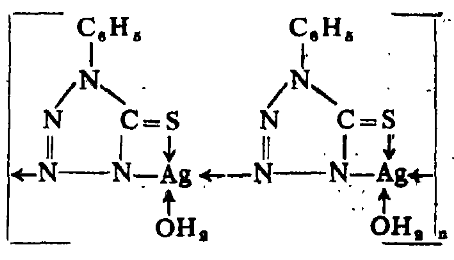


Fig. 4. Probable structure of $[Ag(1PT5T)H_2O]_n$.

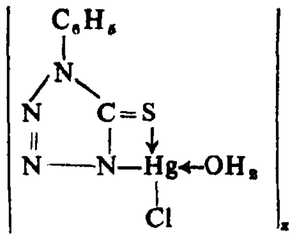


Fig. 5. Probable structure of $[HgCl(1PT5T)H_2O]_x$.

Acknowledgement

Authors are thankful to the authorities of Patna University and U.G.C., New Delhi, for granting U.G.C. Fellowship to D. K. S.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1071-1073

Determination of Thymol in Various Pharmaceutical Formulations by Gas Chromatography

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Manuscript received 19 September 1979, revised 4 August 1980, accepted 25 August 1980

The present work describes a gas chromatographic method to estimate thymol in five different pharmaceutical formulations. Thymol was extracted by chloroform and gas chromatographed using a 2 m × 3 mm I. D. glass column packed with 3% OV-225 on Chromosorb (HP) 80/100 mesh at oven temperature of 170°, injector and detector temperature of 210°. The flow rate of nitrogen (carrier gas) was 32 ml/min., p-chlorophenol was used as an internal standard. The amount of thymol found by the proposed gas chromatographic method ranges between 96.1 to 100.2% of the labelled amount. The percent recoveries for different pharmaceutical formulations were found to be between 99% to 101%.

THYMOL is widely used in various pharmaceutical preparations due to its antibacterial and antifungal activity. It is also valued for its carminative, stimulant and antispasmodic properties.

Grim and Senjkovic[1] have reported a GLC method to estimate thymol from the extract of thymus vulgaric. Porcaro[2] and Moshonas[3] has described a GLC method to determine thymol from essential oils. Matthew[4] has described a GLC method to estimate thymol from blood plasma or serum. No GLC method has been reported in literature to detect or estimate thymol in pharmaceutical formulations which are widely used in practice. In the present work we have developed a simple gas chromatographic method to determine thymol in five different commercially available pharmaceutical preparations.

Experimental

Reagents and solutions : Thymol BP, *p*-chlorophenol 99% pure, sodium carbonate AR grade, sodium hydroxide BDH and chloroform chromatographic grade were used. The following solutions were prepared for GLC analysis.

Standard thymol solution : was prepared by dissolving 50 mg of thymol BP in 50 ml of chloroform in a volumetric flask.

Internal standard : About 300 mg of *p*-chlorophenol (PCP) was weighed accurately, dissolved and made to 100 ml with chloroform. In case of cream and ointment *p*-chlorophenol was dissolved in 0.1*N* sodium hydroxide solution.

Working standard : 1 ml of the standard thymol solution and 1 ml of the internal standard in chloroform were mixed and diluted to 10 ml with chloroform.

Preparation of sample solution for GLC analysis : Sample solutions were prepared from formulations in the forms of tablet, liquid, cream and ointment.

(a) *Tablet :* 20 tablets were crushed, powdered and weight equivalent to two tablets was taken in stoppered flask. 10 ml of chloroform and 20 ml of internal standard solution were added and thymol was extracted in chloroform by vigorous shaking. The mixture was filtered and washed with chloroform. The final volume was adjusted to 50 ml. A 2.5 ml of aliquot was diluted with chloroform to 10 ml.

(b) *Liquid :* A sample equivalent to 2.5 mg of thymol and 5 ml of 5% sodium bicarbonate were mixed well in a separatory funnel. 2.5 ml of internal standard in chloroform and 10 ml of chloroform were added and shaken well. The two layers were allowed to separate and chloroform layer was collected in 25 ml volumetric flask. The aqueous layer was washed twice with 5 ml of chloroform and the washings were added to first extract and the volume adjusted to 25 ml with chloroform.

(c) *Liquid :* A sample equivalent to 6 mg of thymol was taken in a separatory funnel containing 10 ml of water, 25 ml of internal standard in sodium hydroxide was added. The mixture was acidified with dil. hydrochloric acid. This formulation contains 1.2% of free iodine and was removed by adding few drops of sodium thio-sulphate. Thymol was extracted from the mixture by shaking with 25, 10 and 10 ml portions of chloroform. The combined chloroform extract was diluted to 50 ml. 2 ml of aliquot was diluted to 10 ml with chloroform for analysis.

(d) *Cream :* To the sample equivalent to 12 mg of thymol 10 ml of water, 10 ml of 10% sodium hydroxide and 25 ml of internal standard in sodium

hydroxide were added. The mixture was heated on a water bath to melt, mixed well, cooled, filtered and the filtrate diluted to 100 ml with water. 10 ml of the diluted solution was acidified, then sodium carbonate was added to make the solution just alkaline. The alkaline solution was transferred to a separatory funnel and thymol was extracted with successive quantities of 10, 5, 5 ml of chloroform. The combined chloroform extract was diluted to 25 ml with chloroform. In this method thymol was extracted with chloroform in alkaline condition to avoid interference of benzoic acid which was present in the sample.

(e) *Ointment :* Similar procedure as for cream was used. The only difference was that in this case the extraction with chloroform was carried out in acidic condition instead of slightly alkaline one.

Chromatography :

Instrument : Intersmat GC-112 single column gas chromatograph, equipped with flame ionization detector and 1 mv linear recorder was used.

Column : A 2 m × 3 mm I. D., glass column, packed with 3% OV225 on Chromosorb (HP) 80/100 mesh was used for all the determinations.

Operating conditions : Column oven temperature 170°, detector and injection port temperature 210°. The flow rate of carrier gas (nitrogen), hydrogen and air were 32 ml/min, 20 ml/min and 400 ml/min respectively. About 1 μl of working standard solution and sample solutions were injected using 10 μl Hamilton syringe. From the chromatograms the peak heights of thymol and PCP (internal standard) were measured and the amount of thymol were calculated as below :

mg thymol/g or ml of the formulation

$$= \frac{hs \times Rx \times A \times D}{hx \times Rs \times W}$$

where, hx—Peak height of PCP in the chromatogram of sample.

hs—Peak height of thymol in the chromatogram of sample.

Rx—Peak height of PCP in chromatogram of standard solution.

Rs—Peak height of thymol in the chromatogram of standard solution.

A—mg/ml of thymol in standard solution.

W—Weight in g or volume in ml of the formulation taken for analysis.

D—Dilution factor introduced due to the preparation of the sample solution.

Recovery Experiment :

To fixed aliquots of sample solution, the thymol content of which are already determined by the present method, were added three different known levels of thymol, and total amount of thymol per ml or g were determined. Seven repetition measurements per level of added thymol were made. Recovery, which is the difference between thymol found and thymol already present in the aliquot, was expressed as percentage of added thymol, and is given by the equation

$$\% \text{ Recovery} = \frac{(\text{Thymol found} - \text{Thymol already present}) \times 100}{\text{Thymol added.}}$$

The average of these results with standard deviation is present in Table 1.

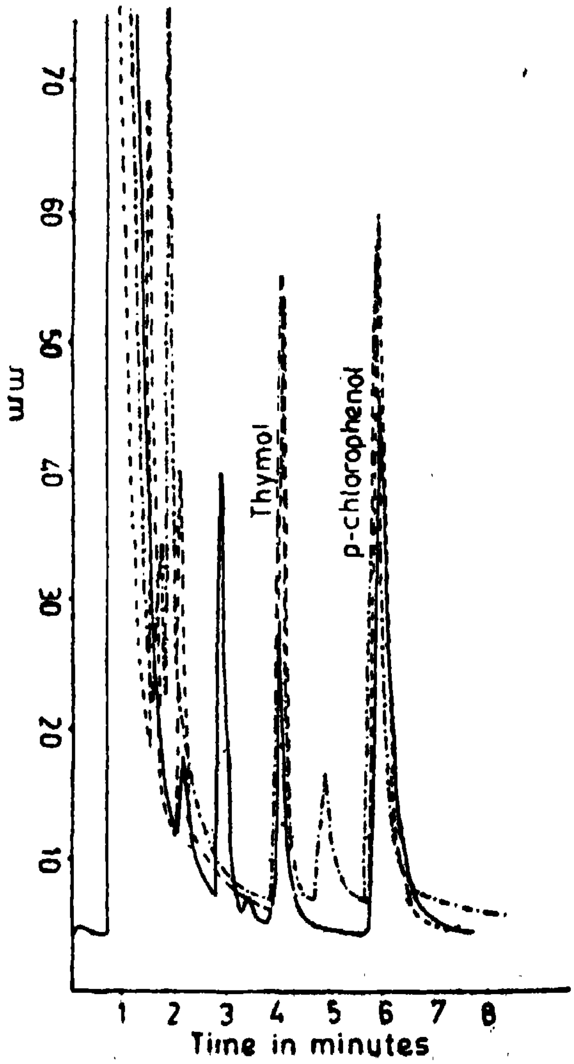


Fig. 1. Chromatograms of Chloroform Extracts of Tablet (—), Liquid (----) and Cream (-·-·-) after suitable treatment.

TABLE 1—AMOUNT OF THYMOL IN DIFFERENT PHARMACEUTICAL FORMULATIONS AS DETERMINED BY THE PRESENT METHOD

Formulations	Thymol present (as per label)	Thymol found (as percentage of labelled amount)	Thymol recovered (as percent of added amount)
Liquid	0.06%	98±0.5%	100±0.5%
Liquid	0.23%	96±1.0%	99±1.0%
Tablet	5.4 mg/tab	100±1.5%	99±1.5%
Cream	0.5%	96±1.1%	99±1.1%
Ointment	1.0%	99±1.2%	101±1.2%

Results and Discussion

Fig. 1 represents typical chromatograms of extracts of tablets, liquid and cream with added internal standard. The facts that peaks due to thymol and the internal standard (PCP) are well resolved and are not interfered by peaks due to other chemicals extracted along with thymol show the adequacy of the internal standard used and the chromatographic conditions and the column chosen for the analysis. Similar chromatograms were obtained with other formulations examined. When the formulations were directly extracted with chloroform and analysed by GLC, serious interference with the thymol and PCP peaks by those due to ingredients like menthol, salicylic acid, benzoic acid, boric acid, camphor, methyl salicylate, cinnamon oil and eucalyptus oil etc. present in the formulation occurred. This interference could be removed by the sample treatments of the sample, as described with Experimental section, before the extraction of thymol by chloroform. The proposed method is quick and simple, GLC peaks were sharp accurate results could be calculated from peak heights. Accuracy of the results is reflected in their closeness with those declared by the manufacturers in the lable (Table 1). Almost quantitative recovery of thymol from a range of pharmaceutical formulation by the extraction procedure (Table 1) shows that the present method can be profitable used in routine analysis of thymol in similar formulations.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1074-1075

Kinetics of the Oxidation of Propyl Mandelate by Molecular Bromine*

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Manuscript received 17 April 1979, revised 18 June 1980, accepted 25 August 1980

The oxidation of propyl mandelate by molecular bromine gives benzaldehyde. The reaction is first order with respect to bromine and follows Michaelis-Manten type of kinetics with respect to substrate. This indicates that the reaction proceeds through the complex between the ester and the bromine. The rate is decreased by the addition of bromide ions only to the extent that the bromide ions convert free bromine into inactive tribromide ions. This confirms that the molecular bromine is the active oxidant species. The effect of solvent composition and acidity dependence of the oxidation rate suggests the base catalysis of the reaction. The energy of activation and entropy of activation have values 11.4±0.6 k cals mole⁻¹ and −39.8±2 cal degree⁻¹ mole⁻¹ respectively. A mechanism which satisfactorily correlates all the experimental facts have been proposed.

THE kinetics of the oxidation of mandelic acid and of ethyl, -*p*-chloro-mandelate with bromine and with hypobromous acid has been studied by Auckett and Barker[1]. These authors conclude that for these reactions molecular bromine is the effective oxidant and that the ester behaves like a secondary alcohol. Our preliminary results on the oxidation of propyl mandelate by molecular bromine showed that the product of this oxidation is benzaldehyde. This indicates that propyl mandelate does not behave as a secondary alcohol as concluded by Auckett and Barker[1]. We have, therefore, investigated the reaction of propyl-mandelate with molecular bromine in greater details. The results of this investigations are given below.

Experimental

(a) *Material used :* Propyl-mandelate was prepared by Fischer Method[2]. Analytic reagent grade bromine was used without further purification. Acetic acid (B. D. H.) was purified by the method described by Eichelberger and LaMer[3]. Other chemicals used were of analytical grade specifications.

(b) *Kinetic measurements :* Because of the limited solubility of propyl-mandelate in water the reaction was carried out in aqueous acetic acid solutions. The reactions were carried out at constant temperature (±0.02°) ; *p*H was adjusted by neutralizing the acetic acid in the solution by sodium hydroxide.

The oxidation capacity of bromine was measured by titration with standardised solution of sodium thiosulphate.

(c) *Product study :* The product study was made under kinetic conditions. The oxidised mixture was completely neutralized by aqueous sodium bicarbonate and then extracted with ether. The ethereal layer was heated on a water bath to remove the ether, cooled, made acidic and 2 : 4,-dinitrophenyl hydrazine (in 2*N* hydrochloric acid) solution was added. The precipitate of 2 : 4,-dinitrophenyl hydrazone derivative was recrystallized and found to have m.p. 236-237° and m.m.p. 235-237°. This shows that benzaldehyde is the product of oxidation

$$PhCH(OH)COOC_3H_7 + Br_2 \longrightarrow PhCHO + C_3H_7Br + CO_2 + Br^-$$

Results and Discussion

The order with respect to bromine is one for nearly 60 percent of the reaction at constant bromide ion concentration. A plot of inverse of first order rate constant versus inverse of ester concentration gives a straight line which cuts the rate constant axis. This indicates a complex formation between ester and bromine. At constant ester concentration the first order rate constant decreases with increase in bromide ion concentration. A plot of inverse of first order rate constant versus bromide ion concentration gives a straight line. This shows that the rate of the reaction can be expressed as :

$$Rate = \frac{k[Ester] \times K'[Br_2]Total}{\{(1/K)+[Ester]\}\{K'+[Br^-]\}}$$

where K is the formation constant of the complex between the ester and bromine and K′ is the dissociation constant for the reaction $Br_3^- \rightleftharpoons Br_2 + Br^-$. From the data given in Table 1 the value of the formation constant K can be estimated. This works

* Presented at Annual convention of Chemists (1977) held at Jaipur.

TABLE 1—EFFECT OF VARIATION OF ESTER CONCENTRATION AND BROMIDE CONCENTRATION ON RATE

Solvent composition : 50 per cent acetic acid
50 per cent water (v/v)

$[Br_2] = 2.0 \times 10^{-3} M$ $pH = 3.3$ Temperature = 35°C

$[Ester] \times 10^{3}$ moles litre^{-1}	$[Br^-]$ moles litre^{-1}	$k_1 \times 10^{5}$ sec^{-1}
2.0	0.05	5.76
2.0	0.10	4.15
2.0	0.15	3.10
2.0	0.20	2.45
4.0	0.05	9.60
6.0	0.05	12.8
8.0	0.05	15.2

out to be 10.9 ± 0.6 mole lit^{-1}. Similarly the dissociation constant K′ can also be estimated from this data, the value of K′ comes out to be 0.058 ± 0.005 moles lit^{-1}. This value of dissociation constant agrees well with the value reported earlier[4]. The effect of bromide ion on rate clearly shows that molecular bromine is the active oxidant under experimental conditions[5].

Increase of pH increases the rate of reaction in the pH range 3.0 to 5.0 (Table 2). At constant pH the rate decreases with increase in the proportion of acetic acid in the solvent mixture (Table 3). These results can be explained on the basis of base catalysis, for the disproportionation of the complex between ester and bromine (hypobromite ester).

TABLE 2—EFFECT OF pH ON THE RATE OF REACTION

Solvent composition : 70 per cent acetic acid
30 per cent water (v/v)

$[Ester] = 2.0 \times 10^{-3} M$ $[Br^-] = 5.0 \times 10^{-3} M$
$[Br_2] = 2.0 \times 10^{-3} M$ Temperature = 35°C

pH	3.3	3.9	4.4	5.0
$k_1 \times 10^{5}$ sec^{-1}	3.20	4.17	5.48	7.49

TABLE 3—VARIATION OF RATE OF REACTION WITH PERCENTAGE ACETIC ACID

$[Ester] = 2.0 \times 10^{-3} M$ $[Br^-] = 5.0 \times 10^{-3} M$
$[Br_2] = 2.0 \times 10^{-3} M$ $pH = 3.3$ Temperature = 35°C

Percentage acetic acid	40	50	60	70
$k_1 \times 10^{5}$ sec^{-1}	7.83	5.76	4.10	3.20

The reaction was carried out at different temperatures (Table 4). The values of energy of activation and entropy of activation for this reaction have been estimated from the temperature effect. These values are $\Delta E^{\neq} = 11.4 \pm 0.6$ k cals mole^{-1} and $\Delta S^{\neq} = -39.8 \pm 2$ cal. degree^{-1} mole^{-1}.

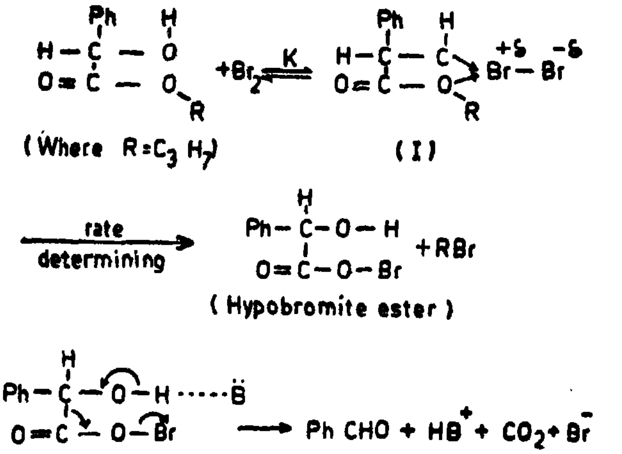
TABLE 4—VARIATION OF REACTION RATE WITH TEMPERATURE

Solvent composition : 70 per cent acetic acid
30 per cent water (v/v)

$[Ester] = 6.0 \times 10^{-3} M$ $[Br^-] = 1.0 \times 10^{-3} M$
$[Br_2] = 1.0 \times 10^{-3} M$ $pH = 3.3$

Temperature °	303	308	315	318
$k_1 \times 10^{5}$ sec^{-1}	4.13	5.30	7.14	10.0

These results can be accommodated on the basis of the following mechanism :



This is probably the first report of the formation of the complex of the ester and the bromine which in a slow irreversible step gives the hypobromite ester of the mandelic acid. The type of complex proposed here is similar to the one proposed by Barker, Overrend and Rees[6] for the reaction of β-D-glucose and bromine. The hypobromite ester of mandelic acid undergoes a base catalysed reaction giving benzaldehyde.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1076-1078

Kinetics of Acid—Base Catalysed Iodination of Cyclic Ketones—II

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Manuscript received 18 May 1979, revised 10 October 1979, accepted 26 August 1980

The kinetics of iodination of cyclic ketones have been studied in different carboxylate buffers and in $HClO_4$ acid in 50% MeOH - water (v/v). The reaction was found to be first order in ketone and catalyst and zero order in iodine. The activation parameters like $\Delta E^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were evaluated. The catalytic constants of propionate, acetate, lactate and glycolate buffers were measured at 35° for each ketone. The Bronsted coefficient 'β' for cyclo-pentanone, cyclo-hexanone, cyclo-heptanone and cyclo-octanone were calculated. The anomalous behaviour of high reactivity of cyclo-pentanone was explained on the basis of I-strain concept. The reactions were also studied in various $HClO_4$ acid concentrations keeping ionic strength constant at 40°. A probable mechanism has been suggested.

THE kinetic studies on the halogenation of aliphatic and aromatic ketones have been reported by a number of workers[1-5] under different conditions. Not much work seems to have been done on the halogenation of cyclic ketones using general base catalyst except the work done by Bell[6] and Jagdale[7].

In continuation of our earlier work on the halogenation of acetophenones[8], we are communicating in this paper the work on iodination of cyclo-pentanone, cyclo-hexanone, cyclo-heptanone and cyclo-octanone in 50% MeOH – water (v/v) with different carboxylate anions as catalysts.

Experimental

All the chemicals used were of AnalaR grade. Cyclo-pentanone (b. p. 130°), cyclo-heptanone (b. p. 179°) were of E. Merck quality and cyclo-hexanone (b. p. 155°) of BDH AnalaR quality was distilled before use. Cyclo-octanone (b. p. 195°) of Koch-light product was used without further purification.

The reaction rates were measured in buffer solutions prepared from NaOH (free from carbonate) and various carboxylic acid solutions in 50% MeOH – water. The concentrations of ketone and iodine were $5 \times 10^{-2} M$ and $5 \times 10^{-3} M$ respectively, with varying buffer concentrations at a fixed buffer ratio (r = 1) in the reaction mixture at a constant ionic strength (μ = 0.8M) maintained by adding $NaClO_4$. The reactions were studied at different temperatures (30 to 50°) with acetate buffer and at 35° with other buffers. A series of reactions were studied with varying acid concentrations keeping ionic strength constant using $NaClO_4$ and the results were interpreted to explain acid and ionic strength effects. The procedure adopted for the measurement of rate constant and calculations were same as in our earlier publication[8].

Results and Discussion

The rates of reactions were found to be first order in ketone, and in catalyst and zero order in iodine. The pseudo first order rate constants at different temperatures in 50% MeOH – water (v/v) and the thermodynamic parameters calculated at 35° are given in Table 1. The thermodynamic parameters indicate the bimolecular nature of reaction and the stabilisation of transition state compared to that in the reactants.

Bronsted Relationship :

The catalytic constants of different buffers were calculated for the 5, 6, 7 and 8 membered cyclic

TABLE 1—RATE CONSTANTS FOR THE IODINATION OF CYCLIC KETONES AT DIFFERENT TEMPERATURES CATALYSED BY ACETATE BUFFER, ACTIVATION PARAMETERS AND BRONSTED COEFFICIENTS AT 35° IN 50% MeOH – WATER (v/v)

[Cyclic ketone] = 0.05M, [Acetate] = 0.5M, [I_2] = $5 \times 10^{-3} M$, μ = 0.8

Cyclic ketones	Rate constant $k \times 10^{6}$ sec^{-1} Temp. 30°C	35°C	40°C	45°C	50°C	$\Delta H^{\neq}$ K. cal/mole	$-\Delta S_{\neq}$ e.u.	'β'
Cyclo-pentanone	35.48	61.17	111.50	202.00	326.20	21.82	7.0	0.88
Cyclo-hexanone	11.28	18.95	33.35	51.82	88.75	19.58	16.8	0.09
Cyclo-heptanone	3.71	5.92	9.45	13.94	22.40	16.65	28.9	0.16
Cyclo-octanone	5.40	10.50	21.85	34.30	70.06	28.88	4.0	0.92

ketones, by plotting observed rate constant versus buffer salt concentration at a given pH in 50% MeOH – water at 35° and are given in Table 2. The ionisation constants of propionic, acetic, lactic and glycolic acids required for these calculations were also determined in 50% MeOH – water (v/v) at 35° using the pH metric method[8]. The plot of logarithm of catalytic constant versus pK_a of acid gave Bronsted plots, and the corresponding Bronsted slopes 'β' for cyclo-pentanone, cyclo-hexanone, cyclo-heptanone and cyclo-octanone were calculated to be 0.33, 0.09, 0.16 and 0.22 respectively. The Bronsted coefficient 'β' provides a measure of sensitivity of the reaction to the basicity of the acid and also on the stability of the ring[17,18].

TABLE 2— CATALYTIC CONSTANTS OF DIFFERENT BUFFERS AT 35°C IN 50% MeOH – WATER(v/v)

[Ketone] = $5\times10^{-2}M$, $[I_2] = 5\times10^{-4}M$, $\mu = 0.8M$, Temp. = 35°C

Buffer	pK_a	Catalytic constant $k_b\times10^4$ l.m^{-1}s^{-1} Cyclo-pentanone	Cyclo-hexanone	Cyclo-heptanone	Cyclo-octanone
Propionate	5.65	147.50	48.50	14.20	29.50
Acetate	5.87	120 00	45.00	115.5	25.00
Lactate	4.57	55.00	36.50	8.40	15.00
Glycolate	4.50	49.10	35.80	8.20	14.40

Acid and Ionic Strength Effect :

The reactions were studied with varying $HClO_4$ acid concentrations in 50% MeOH – water (v/v) at 40° and the observed rate constants are computed in Table 3. The ionic strength was maintained constant for a series of reactions using $NaClO_4$ salt. A plot of k_{obs} against H^+ ion concentration gave linear curves, which prove that enolisation occurs via conjugate acid species and the intercepts indicate that the reaction occurs via neutral species[8]. Since the slope (k_{H^+}) increases with increase in ionic strength the acid catalysed halogenation is subjected to positive salt effect (Table 4).

TABLE 3—DEPENDENCE OF RATE ON [H⁺] AND IONIC STRENGTHS IN 50% MeOH – WATER(v/v)

[Ketone] = 0.01M, $[I_2]$ = 0.005M, Temp. = 40°C

Ionic strength (μ)	$[HClO_4]M$	Rate constant $k\times10^5$ sec^{-1} Cyclo-pentanone	Cyclo-hexanone	Cyclo-heptanone	Cyclo-octanone
	0.025	2.21	7.37	1.47	7.10
0.1M	0.050	4.51	14.86	2.86	14.48
	0.075	7.00	21.57	4.43	21.22
	0.100	8.98	30.40	6.09	30.33
	0.050	—	—	2.92	15.89
	0.100	11.40	36.54	6.41	32.33
0.4M	0.150	—	—	9.80	46.25
	0.200	21.80	65.70	13.08	62.18
	0.300	29.55	94.88	—	—
	0.400	36.68	120.20	—	—
	0.100	12.05	33.78	7.12	32.24
0.8M	0.150	18.11	52.52	10.93	49.17
	0.200	22.42	66.79	15.06	63.00
	0.250	29.70	75.51	18.32	80.74

TABLE 4—CATALYTIC CONSTANTS OF [H⁺] IONS AT DIFFERENT IONIC STRENGTHS IN 50% MeOH – WATER(v/v)

[Ketone] = 0.01M, $[I_2] = 5\times10^{-3}M$, Temp. = 40°C

Ionic strength	Catalytic constant $k_{H^+}\times10^4$ l m^{-1}s^{-1} Cyclo-pentanone	Cyclo-hexanone	Cyclo-heptanone	Cyclo-octanone
μ = 0.1M	9.52	27.80	5.97	28.57
μ = 0.4M	10.17	28.80	6.58	30.67
μ = 0.8M	11.57	33.30	7.45	32.90

Mechanism :

The reactivity of cyclo-pentanone in base catalyst is 3 to 4 times greater than cyclo-hexanone, which is confirmed both from the observed rate constants as well as from Bronsted slopes. According to classical theory cyclo-hexanone can be formed without appreciable strain, while cyclo-pentanone with considerable strain. On this basis cyclo-hexanone should be a stronger acid and more reactive towards halogenation than cyclo-pentanone. But the observation is in opposite direction to that anticipated. Similar anomaly has been observed in case of halogenation of 2-carbethoxy esters[6], but no explanation was given. This may be explained on the basis of I-strain concept. In the enolate ion the hybridisation of α-carbon atom changes from SP^3 to SP^2, four bond oppositions are relieved, hence its strain is decreased. This favours SP^3 to SP^2 transition and corresponding displacement reactions in cyclo-pentanone systems are relatively rapid. In the six membered ring, however, the rigid (chain) form is free of bond oppositions. Change of hybridisation from SP^3 to SP^2 produces bond oppositions and is therefore resisted. Correspondingly displacement reactions in cyclo-hexyl systems are relatively slow. Similar considerations apply to seven membered rings which are also mobile and beset with bond oppositions of adjacent C—H bonds, although to a somewhat lesser extent than the five membered rings.

The medium-sized rings like cyclo-octanone is beset with angle deformations, bond opposition, and trans annular interactions. Most of these are due to hydrogen-hydrogen interreactions, the SP^2 configuration, with its lesser number of C—H bonds is therefore favoured[10] over SP^3. This was confirmed in case of acetolysis of cyclo-alkyl tosylates[11], reaction of cyclo-alkyl bromides with lithium or potassium iodide[12], and solvolysis of methyl cyclo-alkyl chlorides in 80% ethanol [13,14]. The observed rate constants in buffers show that the sequence of halogenation is cyclo-pentanone>cyclo-hexanone>cyclo-octanone>cyclo-heptanone. However, our results indicate some irregularity in case of cyclo-heptanone which is slower than expected. This

indicates that effects other than I-strain may be important, particularly polar factors may also have to be considered. Similar anomalies were observed by Roberts and co-workers[15].

The reactivity order in acid catalysis is cyclo-hexanone ~ cyclo-octanone > cyclo-pentanone > cyclo-heptanone. The sequence is reverse of that observed for base catalysis and is in confirmity with the results of Murthy[16]. Cyclo-heptanone is less reactive even in acid catalyst.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1079-1082

Kinetics of Oxidation of Phenacyl Bromides by Cerium(IV) Sulphate in Acetic Acid and Sulphuric Acid Media

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Manuscript received 2 November 1979, revised 5 July 1980, accepted 7 August 1980

The kinetics of oxidation of phenacyl bromides by cerium(IV) sulphate in acetic acid and sulphuric acid media, obeys first order with respect to phenacyl bromides and also with free [Ce^{4+}]. The reaction was acid catalysed and the participation of water molecule in the rate determining step has been suggested. The reaction is accelerated by electron withdrawing substituents. The order of reactivity was :

p-NO_2 > m-NO_2 > m-Br > p-Br > H

The Hammett's reaction constant is (ρ = 0.5). A mechanism involving free radicals and trimerisation of Ce^{4+} has been suggested for the oxidation of phenacyl bromides.

KINETICS of oxidation of several organic compounds by cerium(IV) has been studied by Richardson[1]. The literature on the oxidation of halo-organic compounds is meagre and recently we have reported the oxidation of phenacyl bromides by vanadium(V) in sulphuric and perchloric acids[2]. These oxidations exhibit first order dependence on substrate as well as on oxidant and follow free radical pathway and absence of water molecule participation in the reaction steps was confirmed through Hammett's acidity and Bunnett's plots. In this paper we are presenting the kinetics of oxidation of several phenacyl bromides (H, p-Br, m-Br, p-NO_2 and m-NO_2) by cerium(IV) sulphate containing acetic and sulphuric acids.

Materials and Methods :

The phenacyl bromide, m-bromo-phenacyl bromide and p-nitrophenacyl bromide were of Fluka, and p-bromophenacyl bromide of Koch—Light and m-nitrophenacyl bromide was prepared by the procedure given by Brooks[3]. The acetic acid used wes AnalaR BDH twice refluxed and distilled with chromium trioxide. The sulphuric acid was of BDH, AnalaR and all other chemicals used were of AnalaR grade. The solutions of phenacyl bromides were prepared by dissolving the required amount in 100% acetic acid and stock solution of cerium(IV) sulphate was prepared by dissolving ceric sulphate in 5*M* sulphuric acid and standardised by standard Fe(II) solution. The methods employed to follow the reaction were same as described earlier[2].

Stoichiometry and product analysis :

The reaction mixtures containing ten times excess of cerium(IV) with respect to each phenacyl bromide was left at 45°, until there was no change in cerium(IV) concentration. It was observed that three moles of cerium(IV) were used per one mole of each phenacyl bromide. Hence the stoichiometric equation can be therefore written as :

$$2X-C_6H_4COCH_2Br+6Ce(IV)+4H_2O \longrightarrow 2X-C_6H_4COOH+2HCHO+6Ce(III)+Br_2+6H^+ \quad \ldots (1)$$

Corresponding benzoic acids obtained from the oxidation products of phenacyl bromides were characterised, by keeping the reaction mixture with little excess of stoichiometric concentration of cerium(IV) with respect to phenacyl bromide in 3*M* H_2SO_4 and 60% (v/v) acetic acid at 45°, till the reaction was complete. The reaction mixture was then extracted with ether. After removing the acetic acid and ether, the solid product so obtained was treated with sodium bicarbonate and filtered. Acidification of the filtrate gave a solid product which after recrystallisation with hot water gave the melting point of corresponding benzoic acid with ±2° variation. Formaldehyde was detected by the chromotropic acid test.

Results

The oxidation reactions for various phenacyl bromides in sulphuric acid medium containing 50-60% (v/v) acetic acid showed first order dependence on [substrate] as well as [Ce^{4+}]. The value k_1/[substrate] remains almost constant, and plot of k_1 versus [substrate] passes through origin indicating that the order with substrate is one. Although the first order plots are linear for all the concentrations of cerium(IV), the rate constant k_1 is not independent of initial [Cerium(IV)]. The rate constant k_1 decreases remarkably with increase of [Cerium(IV)] (results are in Table 1).

Table 2 shows the increase of pseudo-first order rate constants with increase in the concentration of

TABLE 1—DEPENDENCE OF RATE ON [SUBSTRATE] AND [Ce(IV)] AT 45°C AND 60% (v/v) ACETIC ACID

[Substrate] M	[Ce(IV)] M	10^4 k_1 sec^{-1} for different substrates: Phenacyl bromide	p-bromo phenacyl bromide	m-bromo phenacyl bromide	p-nitro phenacyl bromide	m-nitro phenacyl bromide
0.008	0.004	—	1.20	1.56	3.07	2.10
0.010	0.004	1.35	1.62	1.92	4.20	2.50
0.015	0.004	1.77	2.44	2.86	5.85	3.60
0.020	0.004	2.50	3.42	4.08	7.50	4.72
0.030	0.004	3.60	—	5.76	11.61	—
0.020	0.002	—	4.56	5.83	11.80	7.10
0.020	0.006	2.00	2.66	2.80	5.76	3.30
0.020	0.008	1.60	2.00	2.15	4.22	2.50

TABLE 2—DEPENDENCE OF RATE CONSTANT ON [H_2SO_4] CONCENTRATION

[Substrate] = $1.5\times10^{-2}M$, [Ce(IV)] = $4.0\times10^{-3}M$; Acetic acid = 50% (v/v); temperature = 45°C.

10^4 k_1 sec^{-1} at different sulphuric acid, M: 2.0	2.5	3.0	3.5	4.0	4.5	5.0	**
Phenacyl bromide							
0.98	1.10	1.27	1.66	2.07	2.70	3.45	0.45
p-bromo phenacyl bromide							
1.08	1.24	1.66	2.20	2.84	3.64	4.80	0.50
m-bromo phenacyl bromide							
1.19	1.38	1.77	2.40	3.11	4.00	5.37	0.52
m-nitro phenacyl bromide							
1.54	2.17	3.06	4.20	5.80	7.60	9.98	0.56
p-nitro phenacyl bromide							
2.85	3.32	4.49	6.05	8.14	10.10	14.60	0.56

** Slopes of Zucker-Hammett plots, i.e., log k_1 versus $-H_0$.

sulphuric acid. The Zucker-Hammett's[4] plots log k_1 against $-H_0$ were linear with slopes of less than unity and the Bunnett's plot[5] i.e., $-(\log k_1 + H_0)$ against $-\log a_{H_2O}$ were not linear but gives a positive nature of the curve. The plot of log k_1 against log [H^+] is not linear. The values of $-H_0$ and $-\log a_{H_2O}$ at various acidities were taken from Paul and Long[6] and Bunnett[7], assuming that the values do not change upto 50% acetic acid[8,9]. The effect of solvent acetic acid on rate was studied from 40 to 80% (v/v) (Table 3). The increase in rate with increase in acetic acid composition upto 50% (v/v) is negligible but above 50% composition the rate increases considerably.

TABLE 3—DEPENDENCE OF RATE CONSTANT ON [ACETIC ACID]

[Substrate] = 0.01M; [Ce(IV)] = $4\times10^{-3}M$; [H_2SO_4] = 3M; temp. = 45°C

System	10^4 k_1 sec^{-1} at different CH_3COOH % (v/v): 40	50	60	70	80
Phenacyl bromide	0.76	0.84	1.35	2.20	3.20
p-Bromo phenacyl bromide	1.12	1.24	1.62	2.10	2.80
m-Bromo phenacyl bromide	1.28	1.34	1.92	3.34	—
p-Nitro phenacyl bromide	3.40	3.30	4.20	7.10	—
m-Nitro phenacyl bromide	1.60	1.84	2.58	4.30	—

Discussion

Generally α-halo ketones undergo base hydrolysis. If the phenacyl bromide undergoes hydrolysis, it would give phenacyl alcohol and bromide ion. Hence the possibility of acid hydrolysis of various phenacyl bromides in 1M to 5M sulphuric acid in the presence of 50% (v/v) acetic acid was tested. Even after keeping the reaction mixture for several days, there was no formation of bromide ions, indicating absence of acid hydrolysis of phenacyl bromides in the reaction conditions.

The decrease of pseudo-first order rate constant k_1 with increase of [Cerium(IV)] is not unusual (Fig. 1). In the oxidations of citric acid[10], fructose[11] and methanol and ethanol[12] the reasons for the retardation of rate with increasing concentration of cerium(IV) is most probably due to unreactive dimer or because of the formation of a stable Ce^{4+}-substrate complex. Mehrotra *et al*[13,14]

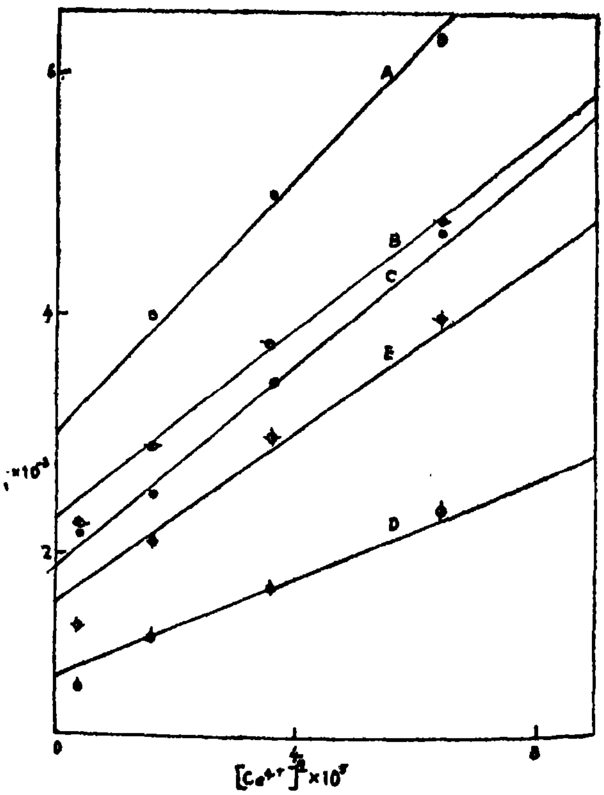


Fig. 1. Plot of [Cerium(IV)]^2 against $1/k_1$
A = phenacyl-bromide;
B = p-Bromo phenacyl bromide;
C = m-Bromo phenacyl bromide;
D = p-Nitro phenacyl bromide;
E = m-Nitro phenacyl bromide.

discussed the probability of dimeric Ce^{4+} in sulphuric acid media, on the basis of well established existence of dimeric Ce^{4+} in perchlorate[16] and nitrate media[16]. From the spectrophotometric study Wiberg and Ford[17] concluded that the principal equilibrium that involved is in between monomeric and trimeric Ce^{4+} in the aqueous acetic acid and perchloric acid media, and also showed that the equilibrium between monomeric and dimeric species is negligible. Hence it may be suggested on the basis of above information and supported by experimental facts that the formation of trimeric Ce^{4+} species in sulphuric acid and acetic acid media may be possible. Due to the formation of trimeric Ce^{4+} species in the reaction the active monomeric Ce^{4+} concentration will decreases considerably and thereby decrease the rate. The rate measurements in sulphuric acid confirm that the reaction is acid catalysed (Table 2). The acceleration in rate with increase in acid concentration might be due to the following equilibria[18].

$$Ce(SO_4)_2 \rightleftharpoons Ce(SO_4)^{2+} + SO_4^{-2} \quad \ldots (2)$$

$$Ce(SO_4)^{2+} + H_2O \rightleftharpoons Ce(OH)(SO_4)^{+} + H^{+} \quad \ldots (3)$$

The Zucker-Hammett's plot of log k_1 against $-H_0$ gave straight lines (Fig. 2, A, B, C, D & E)

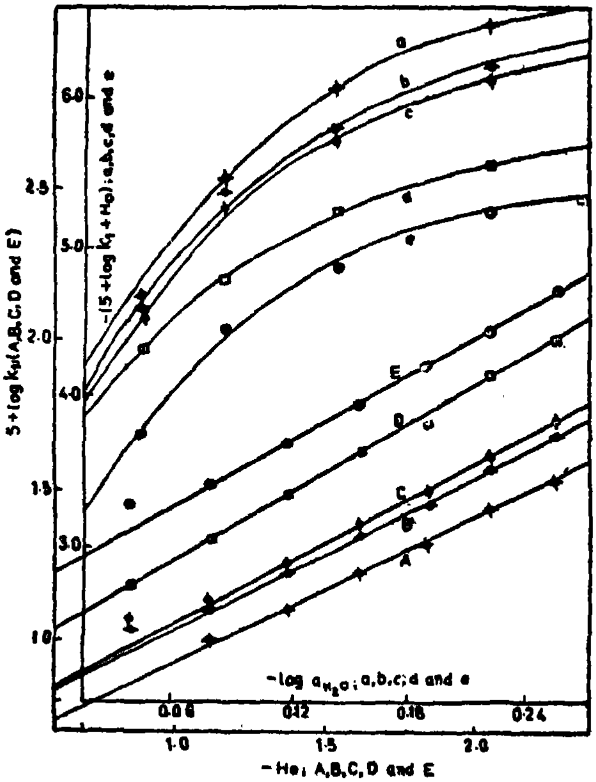


Fig. 2. Dependence of rate on H_0 (Plots A, B, C, D and E) and aH_2O (Plots a, b, c, d and e).
A and a = Phenacyl bromide ;
B and b = p-Bromo phenacyl bromide ;
C and c = m-Bromo phenacyl bromide ;
D and d = m-Nitro phenacyl bromide ;
E and e = p-Nitro phenacyl bromide.

with slopes of 0.45 to 0.55 for the phenacyl bromides, indicating the participation of water molecule in the reaction steps and this is also confirmed by the positive nature of the curve of Bunnett's plots[6]. The rate was not affected upto 50% (v/v) acetic acid. But above 50% (v/v) acetic acid it increases with increasing percentage of acetic acid. This may be due to the increase in the $-H_0$ values of the reaction mixture[8,9].

The following reactions 4 to 8 are the possible steps in the mechanism of oxidations of phenacyl bromides by Ce^{4+} sulphate in 3*M* sulphuric acid containing 50% (v/v) acetic acid. The step 5 is the formation of free radicals, which is considered to be the rate limiting step.

$$3Ce^{4+} \overset{K_1}{\rightleftharpoons} [Ce^{4+}]_3 \text{ trimer} \quad \ldots (4)$$

$$Ce^{4+} + X-C_6H_4COCH_2Br + H_2O \xrightarrow[\text{slow}]{k_2} X-C_6H_4CO^{\cdot} + CH_2OHBr + Ce^{3+} + H^{+} \quad \ldots (5)$$

$$X-C_6H_4CO^{\cdot} + Ce^{4+} + H_2O \xrightarrow{\text{fast}} X-C_6H_4COOH + Ce^{3+} + H^{+} \quad \ldots (6)$$

$$CH_2OHBr + Ce^{4+} \xrightarrow{\text{fast}} HCHO + Ce^{3+} + H^{+} + Br^{\cdot} \quad \ldots (7)$$

$$Br^{\cdot} + Br^{\cdot} \xrightarrow{\text{fast}} Br_2 \quad \ldots (8)$$

The bromine which appeared in the step-8 does not interfere with the method of following the kinetics.

The possible C–C fission in the reaction steps was supported by the final oxidation products, i.e., corresponding benzoic acid and formaldehyde. The rate expression can be written for the above mechanism as :

$$\text{rate} = k_2[Ce^{4+}]_{Free}[X-C_6H_4COCH_2Br]$$

where k_2 is the rate constant. The formation of Ce^{4+} trimer in acetic acid medium was also proposed by Ford and Wiberg[19] in the oxidation of benzaldehyde. Thus, the correlation between the rate law and observed results justified the existence of unreactive trimeric Ce^{4+} species in sulphuric and acetic acid media.

The oxidation of several substituted phenacyl bromides has been studied, and a plot of log k_2 versus the substituent constant, (*H*, *p*-Br, *m*-Br, *m*-NO_2 and *p*-NO_2) was linear with a positive slope. The Hammett's reaction constant has been found to be 0.5. For para-substituents the σ values[20] were taken. The positive value indicates that the rate is

accelerated by the electron withdrawing groups. The order of reactivity was found to be :

$$p\text{-}NO_2 > m\text{-}NO_2 > m\text{-}Br > p\text{-}Br > H$$

The low values of rho indicates the probability of free radicals in the reaction[21]. The formation of the free radicals were also detected by the polymerisation of acrylonitrile when added to the reaction mixture.

Acknowledgement

One of the authors (B.H.K.) wishes to thank the Principal and the management of Lal Bahadur College for the encouragement.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1083-1085

Relative Efficacies of Cationic and Anionic Surfactants and Their Mixtures in the Suppression of Polarographic Negative Maximum of Co(II)

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Manuscript received 16 December 1979, revised 2 July 1980, accepted 25 August 1980

The suppression of polarographic negative maximum of Co(II) has been attempted by various cationic and anionic surfactants viz., cetyl pyridium bromide (CPB), cetyl trimethyl ammonium bromide (CTAB), cetyl dimethyl benzyl ammonium chloride (CDBAC), sodium lauryl sulphate (SLS), dodecyl benzene sulphonate (DBS), dioctyl sodium sulphosuccinate (DSSS), dibutyl sodium sulphosuccinate (DBSS) and tergitol-7. The relative efficacies of these surfactants and their mixtures have been established on the basis of the kinetic parameter αn_a, calculated by Koutecky's method. A comparison of 'αn_a' values at the stage where maximum just disappears gives the relative efficacies of cationic and anionic surfactants and also an insight into their additive or antagonistic influence in the mixture.

RAM *et al*[1] have reported the suppression of polarographic maximum due to Co(II) system by various ionic and non-ionic surfactants and have compared their relative efficacies on the basis of characteristic properties, viz., maximum suppression point[2] (M.S.P.), specific suppression coefficient[3] (S.S.C.) and critical micelle concentration[2] (C.M.C.). Recently, Singh and coworkers[4] have determined the efficacies of various metal ions in the suppression of the negative maximum of Ni(II) in terms of kinetic parameter 'αn_a'. However, this quantitative aspect of the study based on the influence of various ionic and non-ionic surfactants on the kinetics of the irreversible electrode reaction of Co(II) vis-a-vis the suppression of its maximum has not been attempted so far. Moreover, according to Kuta[1,6] very interesting results can be obtained if two surfactants of opposite signs are used as suppressor in their mixture as this would give rise to the additive or antagonistic effects of cationic and anionic surfactants in the suppression of the negative maximum of Co(II). This has not been investigated so far. The present paper deals with the determination of the efficacies of some cationic and anionic surfactants in the suppression of the negative maximum of Co(II), on the basis of the parameter 'αn_a'. Besides this, an attempt has been made to study the additive or antagonistic effects of cationic and anionic surfactants and their mixtures with regard to the suppression of the negative maximum of Co(II).

Experimental

All the chemicals used were of A.R., BDH grade and their solutions were prepared in conductivity water. The depolarizer concentration was kept at $2.0 \times 10^{-3} M$. $NaNO_3$ (0.1 *M*) was used as the supporting electrolyte. A manual polarograph (Toshniwal CL02) in conjunction with a polyflex galvanometer (Toshniwal PL 50) was used for measuring the potential and current respectively. Deoxygenation of the solutions was done by passing through the solution a steady stream of purified nitrogen gas. All the measurements were made at $25 \pm 0.1°$. Saturated calomal electrode (S.C.E.) was used as a reference electrode. The d.m.e. had the following characteristics : $m = 1.673$ mg/sec, $t = 4.04$ sec, $m^{2/3} t^{1/6} = 1.778$ $mg^{2/3} sec^{-1/2}$, $h_{corr} = 63.0$ cm.

Results and Discussion

After the suppression of maximum by the requisite amounts of the surfactants, Co(II) yields, in each case, a well-defined diffusion-controlled wave. On applying various criteria of irreversibility[5-8], it has been ascertained that the electrode reaction of Co(II) is totally irreversible in presence of different amounts of cationic and anionic surfactants as well as their mixtures. The value of the kinetic parameter αn_a has been calculated by Koutecky's method[9].

From Table 1 it is evident that αn_a tends to decrease with the increase in the concentration of each surfactant. αn_a values (and subsequent estimation of α) give a measure of the extent to which kinetics of the electrode reaction is influenced. An attempt to estimate n_a (the number of electrons, involved in the rate determining step) leads to a conclusion that n_a is equal to 2. However, according to Meites[10] only a single electron can be transferred

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at a time and a value of n_a exceeding 1 would not necessarily mean that two electrons are actually added simultaneously but merely indicates that the successive steps occur simultaneously and cannot be distinguished on the time scale implicit in the polarographic measurement. Since the decrease in αn_a values is indiscrete and at no stage the two consecutive values vary by a factor of 2, the possibility of decrease in the value of the product αn_a due to the change in n_a is ruled out. Thus it can be concluded that the value of α is decreasing[11]. α, the transfer coefficient. signifies[12] the fraction of the applied voltage which favours the cathodic reaction, $Co^{2+} + 2e \rightarrow Co$. A decrease in the value of α thus implies that the transfer of electron/electrons is made increasingly difficult. In other words, the electrode reaction is rendered increasingly more irreversible. A decrease in i_d and a negative shift in $E_{1/2}$ with an increase in the concentration of both the cationic and anionic surfactants lend support to this conclusion.

Relative efficacies of surfactants in terms of αn_a values :

At the stage where the polarographic maximum due to Co(II) system just disappears, the order of αn_a value signifies the extent to which the addition of cationic and anionic surfactants renders the electrode reaction more irreversible compared to that in the absence of these surfactants. In other words, a surfactant for which αn_a has got higher value at the point of just suppression will be more effective with minimum influence on the kinetics of the electrode reaction. In the present study the order of αn_a values for different surfactants is as follows :

Cationic : CTAB > CDBAC

Anionic : Tergitol-7 > DBS > DBSS > SLS > DSSS

Thus among the cationic surfactants CTAB eliminates the maximum of Co(II) with minimum influence on the kinetics of the electron transfer than CDBAC. On the other hand among the anionic surfactants Tergitol-7 eliminates the maximum with minimum influence on the kinetics of the electron transfer followed by DBS, DBSS, SLS and DSSS.

A comparison of αn_a values at the point of just suppression in respect of the mixtures of cationic and anionic surfactants shows that in the mixtures of CTAB and SLS, CTAB and DSSS and CDBAC and DSSS, the value of αn_a is larger in comparison to its value when these surfactants are added separately. From this it follows that the influence of CTAB and SLS and those of DSSS with CTAB and CDBAC is additive as they eliminate the maximum of Co(II) with less influence on the kinetics of the electrode process. On the other hand in mixtures of CTAB and DBS CTAB and Tergitol-7, CDBAC and DBS, and CDBAC and DBSS, the value of αn_a is larger in comparison to cationic surfactants (CTAB and CDBAC) while it is lesser than the anionic ones (DBS, DBSS and Tergitol-7). From this it follows that the influence of CTAB and DBS, CTAB and Tergitol-7, CDBAC and DBS and CDBAC and DBSS in their mixtures is antagonistic.

A comparison of αn_a values for cationic and anionic surfactants reveals that these are higher for anionic surfactants than the cationic ones. From this it follows that anionic surfactants suppress the negative maximum of Co(II) with lesser influence on the kinetics of the electron transfer.

The effects of surfactants on electron-transfer processes- that is, on the reversibility of an electrode reaction and on the parameters αn_a and $k^{\circ}_{f,h}$ for irreversible electrode reactions—result[13] from the changes in the structure of the double layer. The adsorbed molecules displace ions from the Helmholtz layer, thereby altering the charge distribution. They may also displace the reaction surface away from the electrode. Both the effects alter the potential at the reaction surface. In addition, a bridge that may serve to effect electron transfer from the electrode to an ion or molecule at the reaction surface when the surfactant is absent may become difficult to envisage when it is present ; the entire mechanism of the electron-transfer process may change.

A decrease in i_d and a negative shift in $E_{1/2}$ (vide Tables 1 and 2) with increasing concentrations of surfactants indicate[14] the inhibition of the electrode process of Co(II). This is due[15] to the increase in surface-coverage of the electrode (d.m.e.).

TABLE 1—POLAROGRAPHIC CHARACTERISTICS DUE TO Co(II) SYSTEM IN PRESENCE OF SURFACTANTS

Surfactant	i_d μA	$-E_{1/2}$ V (S.C.E.)	$D \times 10^6$ cm^2/sec	αn_a
Cationic				
CPB($1.0 \times 10^{-5} M$)	wave drawn out			
CTAB(* $5.0 \times 10^{-5} M$)	14.44	1.27	8.27	0.49
($1.0 \times 10^{-4} M$)	13.68	1.29	7.42	0.46
CDBAC(* $2.0 \times 10^{-5} M$)	13.30	1.32	7.01	0.48
($2.0 \times 10^{-4} M$)	11.40	1.33	5.15	0.46
Anionic				
SLS(* $7.0 \times 10^{-5} M$)	12.92	1.33	6.62	0.74
($1.5 \times 10^{-3} M$)	12.16	1.36	5.86	0.59
DBS(* $2.4 \times 10^{-5} M$)	11 98	1.28	5.56	0.92
($1.4 \times 10^{-3} M$)	10.77	1.29	4.60	0.82
Tergitol-7(* $4.4 \times 10^{-6} M$)	13.68	1.31	7.42	0.96
($8.4 \times 10^{-6} M$)	12.16	1.32	5.86	0.92
DSSS(* $4.0 \times 10^{-4} M$)	15.58	1.37	9.68	0.53
($1.2 \times 10^{-3} M$)	14 44	1.40	8.27	0.51
DBSS(* $8.0 \times 10^{-3} M$)	15.50	1.34	9.58	0.77
($1.4 \times 10^{-2} M$)	13.68	1.37	7.42	0.74

* Indicates the concentration of surfactant at which the maximum just disappears.

TABLE 9—POLAROGRAPHIC CHARACTERISTICS DUE TO Co(II) SYSTEM IN PRESENCE OF SURFACTANT MIXTURES

Surfactant Mixture		i_d μA	$-E_{1/2}$ V (S.C.E.)	$D \times 10^6$ cm^2/sec	αn_a
CTAB (*2.0×10^{-5} *M*)+SLS	(1.0×10^{-3} *M*)	15.20	1.37	9.16	0.96
„ (1.0×10^{-4} *M*)+ „	(5.0×10^{-3} *M*)	13.68	1.40	7.42	0.87
CTAB (*2.0×10^{-5} *M*)+DBS	(1.0×10^{-3} *M*)	14.82	1.39	8.71	0.77
„ (1.0×10^{-4} *M*)+ „	(5.0×10^{-3} *M*)	10.26	1.40	4.17	0.74
CTAB (*1.0×10^{-4} *M*)+Tergitol-7	(6.0×10^{-3} *M*)	10.26	1.29	4.17	0.74
„ (5.0×10^{-4} *M*)+ „	(1.4×10^{-3} *M*)	8.74	1.29	3.03	0.72
CTAB (*3.4×10^{-5} *M*)+DSSS	(3.4×10^{-3} *M*)	15.58	1.41	9.63	0.82
„ (7.4×10^{-5} *M*)+ „	(5.4×10^{-3} *M*)	12.92	1.42	6.62	0.77
CDBAC(*1.0×10^{-5} *M*)+DBS	(1.2×10^{-3} *M*)	13.68	1.37	7.42	0.74
„ (1.0×10^{-4} *M*)+ „	(6.0×10^{-3} *M*)	12.16	1.41	5.86	0.60
CDBAC(*2.0×10^{-5} *M*)+DSSS	(7.0×10^{-4} *M*)	12.92	1.36	6.60	0.98
„ (1.2×10^{-4} *M*)+ „	(2.0×10^{-3} *M*)	12.54	1.38	6.23	0.92
CDBAC(*1.2×10^{-5} *M*)+DBSS	(4.0×10^{-3} *M*)	15.58	1.31	9.63	0.57
„ (3.2×10^{-5} *M*)+ „	(1.2×10^{-2} *M*)	13.68	1.34	7.39	0.56

* Indicates the concentration of surfactants at which the maximum just disappears.

Acknowledgement

Thanks are due to the Principal, Agra College, Agra for providing necessary facilities.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1086-1088

Studies on Surface Tension of Strontium Soaps in Aqueous 2-propanol at 35°

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Manuscript received 17 December 1979, revised 30 July 1980, accepted 25 August 1980

The surface tension of strontium soaps in aqueous 2-propanol has been measured at 35° and the data have been discussed on the basis of Langmuir's approximate equation: $\gamma=\gamma_o(1+X \ln Y)-X\gamma_o \ln C$. Constants X and Y have been calculated for soap systems. Constant X is found to be independent of solvent composition in the mixture but it increases with increasing chain length of soaps. The values of Y show a marked change at 50% 2-propanol concentration which confirms that the change in nature of micelles takes place at about 50% 2-propanol concentration. The surface areas covered by 1 mol of the soaps have been evaluated.

SURFACE TENSION measurement has been used[1-5] for determining critical micelle concentration of surface active substances due to its accuracy for determining the inflection which is nearly the same for longer chain substances because surface tension changes over nearly the same magnitude. The values of CMC of calcium soaps in aqueous methanol are found[6] to be independent of methanol concentration. The surface tension studies[7-9] of barium soaps in aqueous 1-propanol have shown that the change in the nature of micelles from hydrophilic oleo micelle to lipophilic hydro micelle takes place at about 50% 1-propanol. Recently the conductance behaviour of strontium soaps in aqueous 2-propanol has indicated[10] the presence of micelles in the solution and therefore, it appears desirable to measure the surface tension of these strontium soaps (Valerate, Caproate and Caprylate) solution to find out the surface behaviour and nature of micelles formed under different conditions.

Experimental

The chemicals were purified and the soaps were prepared by the methods described in the previous communication[10]. The surface tension of soap solutions was determined by stalagmometer in thermostatically controlled (35±0.05°) bath. The densities were measured with a dilatometer calibrated with conductivity water. The accuracy of the results was checked by determining the surface tension of known solutions. The surface tension results are in dynes cm^{-1}.

Results and Discussion

Surface tension, γ of soap solutions decreases with increasing soap concentration which is due to the decreasing effects in the surface energy of the solvent mixture. This indicates the surface active behaviour of soaps. The plots (Fig. 1) of γ vs C show a sharp change at CMC[10] which is independent of the solvent composition. Surface tension of soap solutions at first decreases rapidly upto 50%, then remains constant upto 60% and finally decreases

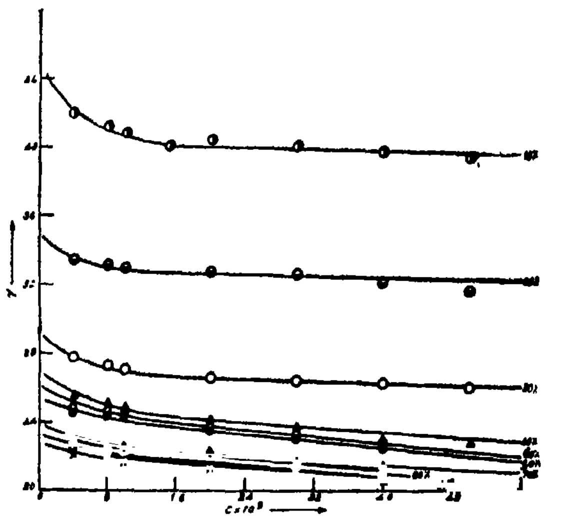


Fig. 1. Plots of surface tension vs concentration of strontium valerate in water 2-propanol mixture at 35°.

with increasing 2-propanol concentration. The plots (Fig. 2) of surface tension vs volume percent of 2-propanol show a change in the behaviour at 50% concentration which has also been observed earlier[10].

Surface tension data have been interpreted using following equation

$$\gamma/\gamma_o=1-KT\,\eta_s/\gamma_o \ln(1+\eta_a/K) \quad \ldots \text{(i)}$$

where η_s is the number of exposed solvent sites per cm^2 of its surface, η_a is the concentration of the

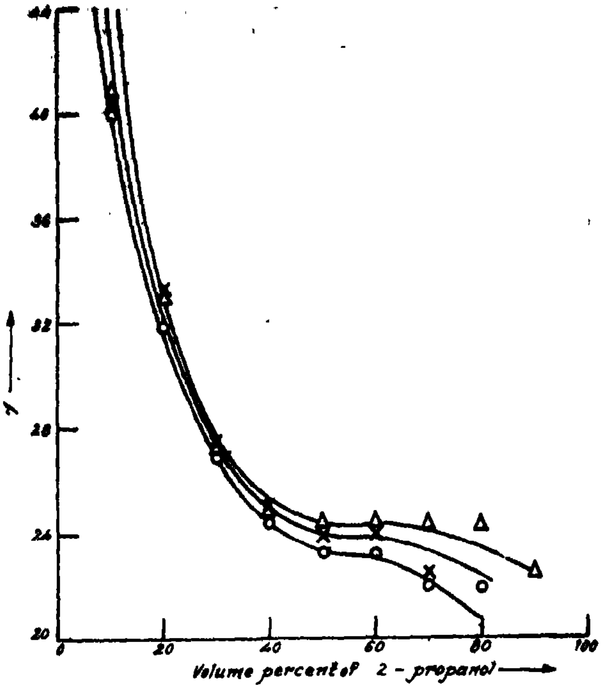


Fig. 2. Plots of surface tension vs volume percent of 2-propanol at 35°.
× —0.004*M* strontium caprylate,
○—0.015*M* strontium caproate,
Δ—0.010*M* strontium valerate.

substrate molecule cm^{-1} in bulk, K is a constant for solvent and other terms have their usual significance.

On substituting

KT $\eta_s/\gamma_o = X$ and $\eta_s/K = C/Y$ one obtains

$$\gamma/\gamma_o = 1 - K \ln (1 + C/Y) \quad \ldots \quad (ii)$$

where γ and γ_o are surface tensions of solutions of concentration C and pure solvent respectively. X and Y are constants. On applying the condition C/Y >>> 1, the following approximate expression which Langmuir showed to apply at high solute concentration and in condition of surface saturation was obtained.

$$\gamma = \gamma_o (1 + X \ln Y) - X \gamma_o \ln C \quad \ldots \quad (iii)$$

The plots (Fig. 3) of γ vs log C are linear which shows that the empirical equation (iii) is applicable to mixed systems also. The values of X and Y have been calculated from the linear plots and are summarised in Tables 1 and 2.

Constant X (Table 1) increases with increasing concentration of 2-propanol upto 60% in the solvent mixture and then decreases at higher concentrations. The values of X also increase with increasing chain length of soap. Since γ_o decreases with increasing

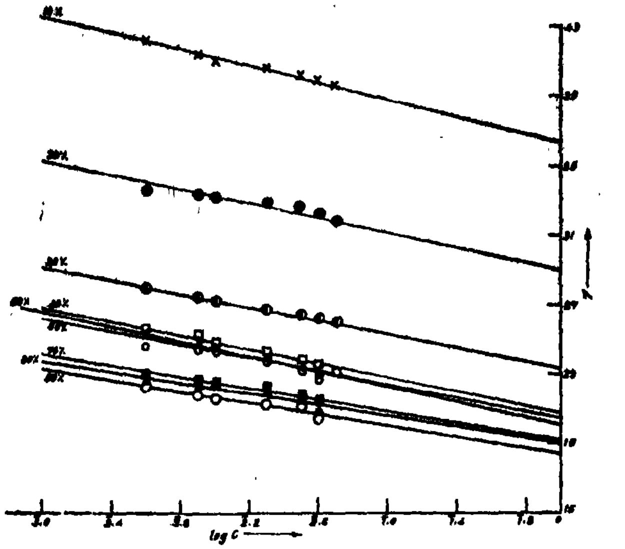


Fig. 3. Plots of surface tension vs log concentration of strontium valerate in water 2-propanol mixture at 35°.

Table 1—Values of X for Strontium Soaps in Aqueous 2-Propanol at 35°C

Volume % of 2-Propanol	$X.10^{3}$ Caprylate	Caproate	Valerate
10	3.254	2.847	2.542
20	3.635	3.115	2.865
30	3.658	3.419	3.263
40	3.736	3.566	3.388
50	3.793	3.618	3.441
60	3.821	3.801	3.473
70	3.776	3.587	3.398
80	—	3.473	3.067

Table 2—Values of Y for Strontium Soaps in Aqueous 2-Propanol at 35°C

Volume % of 2-Propanol	$Y.10^{3}$ Caprylate	Caproate	Valerate
10	0.543	0.782	8.041
20	2.759	3.617	9.376
30	2.460	3.032	6.934
40	2.382	2.773	4.132
50	1.991	2.601	2.339
60	1.514	2.810	3.162
70	1.580	4.383	6.223
80	—	4.949	6.982

concentration of 2-propanol in the water, the number of exposed solvent sites cm^{-2} should decrease for constant value of X. But the variation of values of X shows that number of exposed solvent sites cm^{-2} increase with increase in concentration of 2-propanol upto 60% and decreases at higher concentrations of alcohol. In other words, the concentration of soap molecules in the bulk increases with increase in content of 2-propanol and decreases at higher concentrations (>60%). This occurs due

to change in the nature of micelles from hydrophilic oleo micelles to lipophilic hydromicelles in the soap solutions when the chain length of soap increases the number of exposed solvents sites cm^{-2} increases and therefore chance of micellization increases. This is also evident from the CMC values of strontium soaps, i.e., 0.015, 0.010 and 0.008 *M* respectively for valerate, caproate and caprylate.

The values of γ decrease with increasing volume percent of 2-propanol upto 50% and show an increase at higher concentration of alcohol. Y also decreases with increasing chain length of soaps.

Differentiating equation (iii)

$$d\gamma/d\ln C = -X\gamma_o \quad \text{.. (iv)}$$

On substituting this value in Gibb's adsorption equation the excess concentration of the solute per unit area of the surface Γ is found

$$\Gamma = -\frac{1}{RT} \cdot \frac{d\gamma}{d\ln C}$$

$$\Gamma = \frac{X\gamma_o}{RT} \quad \text{... (v)}$$

Hence the surface area, A covered by the soap micelle formed by 1 mole of the soap is

$$A = \frac{1}{\Gamma} = \frac{RT}{X\gamma_o} \quad \text{... (vi)}$$

The surface area, A occupied by the micelle formed by 1 mole of the soap has been calculated and is given in Table 3. It is observed that the surface area, A of soap micelles depends only on the surface tension of water-2-propanol mixture which decreases with the increase in the surface area. The increase in the size of the micelle occurs due to incorporation of alcohol in the micelle. It is observed that the surface area decreases with increase in chain length of soap.

TABLE 3—VALUES OF A FOR STRONTIUM SOAPS IN AQUEOUS 2-PROPANOL AT 35°C

Volume % of 2-Propanol	$A \cdot 10^{-10}$ cm^2		
	Caprylate	Caproate	Valerate
10	1.845	2.118	2.861
20	2.107	2.490	2.658
30	2.508	2.688	2.810
40	2.683	2.810	2.951
50	2.744	2.880	3.026
60	2.688	2.688	2.951
70	2.978	3.107	3.269
80	—	3.258	3.690

Acknowledgement

The authors are thankful to Dr. K. N. Mehrotra for his keen interest throughout the work and the college authorities for providing laboratory facilities.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1089-1091

Solvent Effect on Ion-Dipole Type of Reactions : Acid Hydrolysis of Ethyl Formate in DMSO—Water Medium

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Manuscript received 24 September 1979, revised 7 May 1980, accepted 7 August 1980

The rate of acid catalysed hydrolysis of ethyl formate has been studied in aqueous DMSO of composition ranging from 0 to 60% of DMSO at temperatures varying from 20° to 40°. The rate is found to increase initially with maxima at about 9 mole percent of DMSO and then decreases on further addition of the organic component. The enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) have been evaluated using the equation of Wynne Jones and Eyring. The non-linearity of ΔH^* and ΔS^* with increasing mole % of DMSO are indicative of definite solvation changes taking place in the medium. The variation in free energy of activation (ΔG^*) values with increasing mole % of DMSO were found to be almost negligible. The variations of the rate constant and the activation parameters have been explained on the basis of solvent-solute interaction, solvation of the transition state and the dielectric behaviour of the medium.

STUDY of the solvent effect of aprotic solvent on the reactions such as hydrolysis of esters and amides have been carried out by a number of workers[1-5], but the explanations put forward are not quite satisfactory.

According to the theory of Parker[6], the rate of such reactions in which the transition state passes through large polarisation should be faster in aprotic solvents than in protic solvents. This contention of Parker was subsequently supported by Roberts[4,7] who studied the alkaline hydrolysis of a large number of esters in DMSO-water mixtures and observed the enhancement of the rate by increasing ratio of aprotic component of the binary solvent mixture. However, this goes against the qualitative prediction of Hughes and Ingold[8] as well as the theoretical prediction of Laidler and Landskroener[9]. Accor ding to them the rate of such reactions should increase with increasing dielectric constant of the medium.

Therefore, in the opinion of the authors more investigations are needed to arrive at a definite conclusion. Primarily with this view and also to find out the activation parameters to study the mechanism of the rate processes, it has been decided to study the rate of hydrolysis of a very simple ester ethyl formate in DMSO-water mixtures which has not been studied so far.

Experimental

Ethyl formate (BDH quality) was distilled. Standard solution of A. R. grade HCl (0.01*M*) was prepared in solvent mixtures of extrapure DMSO varying from 5-60% in double distilled water. The above solution was thermostated in a bath controlled within ±0.5°. After 15 minutes 1 ml of ethyl formate was added to the above thermostated solution. 10 ml aliquot of the reaction mixture at a definite interval of time was removed and quenched in ice-cold water and titrated by standard Baryta solution. Reproducible results were always obtained.

The specific rate constants calculated in various solvent mixtures at temperatures 20°, 25°, 30°, 35° and 40° are shown in Table 1. The table also includes the dielectric constant values interpolated from the curve using the data of Wolford[8].

Results and Discussion

The rate of acid catalysed hydrolysis of ethyl formate in various DMSO-water mixtures at temperatures varying from 20° to 40° has been listed in Table 1. The composition of solvent has been varied from 0 to 60% v/v of DMSO.

It is very interesting to note that the rate of hydrolysis of ester increase no doubt with increasing mole percent of DMSO in the beginning as expected on the basis of the theory put forward by Parker[6] but it comes to a maximum and then the specific rate starts falling. The maximum which is obtained by plotting log k values against solvent composition was found to be 8.82 mole percent of DMSO (corresponding to 27.68% of DMSO by volume) at all the temperatures. The finding supports the contention that both solvent solute interaction and the dielectric effect are imperative and none can be neglected. The inference made by Gelles *et al*[10] that a solvent solute interaction is the more probable factor influencing the rate, the

TABLE 1—RATE CONSTANT OF ACID HYDROLYSIS OF ETHYL FORMATE IN DMSO-WATER MIXTURES AND THE CORRESPONDING DIELECTRIC CONSTANTS

Percentage (v/v) of DMSO	20°C		25°C		30°C		35°C		40°C	
	$k \times 10^4$ min^{-1}	D	$k \times 10^4$ min^{-1}	D	$k \times 10^4$ min^{-1}	D	$k \times 10^4$ min^{-1}	D	$k \times 10^4$ min^{-1}	D
0%	10.55	80.15	16.17	78.30	24.55	76.33	36.33	74.83	54.17	73.18
5%	10.88	80.08	16.64	78.20	25.59	76.43	37.85	64.73	55.38	73.08
10%	11.39	79.93	17.37	78.05	26.06	76.33	38.79	74.63	57.88	72.93
15%	11.98	79.76	18.05	77.85	27.12	76.17	40.11	74.50	59.41	72.83
20%	12.35	79.60	18.75	77.70	28.07	76.00	41.50	74.30	61.46	72.60
30%	13.04	78.98	19.64	77.10	29.54	75.40	43.31	73.70	64.06	72.00
40%	11.94	78.00	17.82	76.05	26.92	74.40	39.81	72.75	59.23	71.10
50%	10.26	76.40	15.58	74.55	23.50	72.86	35.32	71.25	51.88	69.55
60%	8.22	74.00	12.59	72.30	19.38	70.70	29.17	69.10	43.90	67.50

TABLE 2—CALCULATED VALUES OF ΔH^* IN K cal/mole, ΔG^* IN K cal/mole AND $-\Delta S^*$ IN cal/deg/mole IN DIFFERENT SOLVENT MIXTURES

% of DMSO (v/v)	ΔH^*	20°C		25°C		30°C		35°C		40°C	
		ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
0%	14.35	23.52	31.30	23.68	31.31	23.83	31.30	24.00	31.33	24.15	31.31
5%	14.30	23.50	31.40	23.66	31.41	23.81	31.40	23.98	31.42	24.13	31.42
10%	14.25	23.47	31.47	23.63	31.48	23.80	31.49	23.96	31.50	24.11	31.48
15%	14.17	23.45	31.67	23.61	31.69	23.77	31.70	23.73	31.71	24.09	31.70
20%	14.08	23.43	31.89	23.59	31.90	23.75	31.91	23.91	31.92	24.07	31.90
30%	13.98	23.40	32.18	23.56	32.16	23.72	32.15	23.89	32.17	24.04	32.15
40%	14.03	23.45	32.07	23.61	31.12	23.78	32.11	23.94	32.11	24.09	32.09
50%	14.24	23.53	31.73	23.70	31.75	23.86	31.76	24.01	31.74	24.17	31.75
60%	14.70	23.66	30.59	23.83	30.62	23.97	30.61	24.13	30.62	24.28	30.60

dielectric constant becoming only a secondary factor, may be correct in certain cases, but it is not a general feature. The variation of rate constant with increasing mole percent of organic co-solvent in our case clearly shows that the factors influencing the rate are of two types. While one type increases the rate the other type hinders its progress and naturally the observed rate will depend on their relative magnitude. Now the possible factor increasing the rate is the solvation changes of reactants and the transition state. Aqueous DMSO medium has been termed as TNAN type of binary mixtures as reported in the various communications[11]. Intermolecular association of this solvent often occurs in such type of binary mixtures. Packer and Tomilinson[12] have pointed out the breakdown of water-water interaction by adding DMSO as a co-solvent in it. Therefore due to strong tendency of DMSO to break down the water-water interaction to its aqueous binary mixtures, it is quite possible that it may enter into the "structure broken" region of the solvation sheets of the different ionic species. Also DMSO being a dipolar aprotic solvate by ion-dipole type of mechanism, the transition state being large cation is likely to be solvated more than the initial state. This change in solvation will decrease the activation energy (which is apparent from ΔE or ΔH^* values) and thereby increase the rate. This accounts for increase of the rate in beginning. The factor decreasing the rate is quite probably the decrease of bulk dielectric. The increase of DMSO in the binary solvent mixture decreases the bulk dielectric on account of its low value compared to water. This decrease of dielectric constant may lower the concentration of highly polar transition state and thereby decreases the rate. While the former effect is more predominating in the beginning causing an increase in the rate, the latter effect outweighs the former after 8.82 mole percent causing uniform decrease in the rate.

The activation parameters for the acid catalysed hydrolysis of ethyl formate were calculated using Wynne-Jones and Eyring equation[13] in the following form :

$$\log \frac{k}{T} = \left(\log \frac{k}{h} + \frac{\Delta S^*}{2.303R}\right) - \frac{\Delta H^*}{2.303RT}.$$

From the plot of $\log \frac{k}{T}$ against $\frac{1}{T}$ the values of ΔH^* and ΔS^* were obtained. The values of ΔG^* were then obtained by the thermodynamic relation :

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

It was further observed that the values of E_{exp} obtained by Arrhenius equation was nearly equal to ΔH^* values within the limit of precision. These thermodynamic parameters have been tabulated in Table 2. On perusal of the data in the table, the

continuous decrease in the ΔH^* values in the beginning followed by an uniform increase on addition of DMSO is apparent. Although this small variation may not be taken for the minimum considering the magnitude of errors inherent in the estimation, but the non-linearity in ΔH^* values with increasing mole percent of DMSO is quite clear and is indicative of definite solvation taking place in the medium according to Saville and Hudson[14].

Again it is observed further that there is decrease in ΔS^* also in the region. This means that the conversion of initial state in the transition state is accompanied by entropy decrease which is in conformity with the assumption that the transition state becomes more and more solvated compared to initial state as the mole per cent of DMSO is increased. However, the variation in free energy of activation ΔG^* is considerably small and can be taken as nearly constant. Therefore, in general the variation of rate constants as well as most of the activation parameters is explained on the basis of solvent solute interaction, solvation of the transition state and the dielectric behaviour of the medium.

However, further researches are in progress to apply the results of this investigation in testing the various methods and equations[5,15-17] suggested from time to time for evaluating the size b^* of Laidler-Landskroener equation.

Acknowledgement

The authors are grateful to University Grants Commission, New Delhi for awarding a Teacher Fellowship to one of them (R. T. S.).

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1092-1097

Thermo-Osmosis and Higher Order Symmetries*

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Manuscript received 12 April 1979, revised 31 March 1980, accepted 25 August 1980

An attempt has been made to obtain a non-linear phenomenological relation between fluxes and forces for the mass transport of matter and the transport of heat energy in *thermo-osmosis as viewed from the* physical parameters of the classical theory. Poiseuillean flow for fluids (liquids and gases) through membrane capillaries has been taken into consideration for such an attempt. Occurrences of higher order symmetries have also been examined and observed in the present study.

IN continuation of our earlier studies[1,2] for higher order symmetries[3-7], we now examine thermo-osmosis. Known physical parameters of classical theory has been used as a tool. Some such attempt has been made earlier by Rastogi and others[8(a)] for the Knudsen flow of gases through membrane capillaries. Our line of approach is, however, entirely different. It deals with the Poiseuillean flow of matter, a fluid (liquid or gas), through the membrane capillaries and the flow of thermal energy by two methods : Convection and Conduction.

For any Markoffian† process, the local fluxes J_i are the functions of local forces X_i, the intensive parameters a_i and the structural factor G. Hence,

$$J_i = f(X_1 X_2 \ldots\ldots, a_1 a_2 \ldots\ldots, G).$$

G is a factor which takes into account the characteristics of the system. For illustration we may consider fluid flow through a capillary or a tube. The flow depends upon the temperature, T, pressure, P, pressure difference, ΔP and temperature difference, ΔT. In addition, the flow depends on structural factor, G, which is a function of the length and diameter of the capillary.

The basic foundation of the thermodynamics of irreversible processes[9,10], is Gibb's equation, linear phenomenological law and the Onsager's reciprocity relations. The domain of validity of linear laws is smaller as compared to that of the Gibb's equation for entropy production provided the non-linear form of the phenomenological equation can be determined[1,8(b)]. Progress in statistical mechanics[11,12] is still limited and does not yet permit the formal development of a microscopic thermodynamic theory in the non-linear range. The present communication is an attempt to obtain a non-linear phenomenological equation for thermo-osmosis of a fluid (liquid or gas) for the Poiseuillean flow.

The thermodynamic theory of irreversible processes[9-10] gives[10,12] the following rate-equation for thermo-osmosis of a fluid (liquid or gas) in the linear range

$$J_M = L'_{11}(-v\Delta P'/T) + L'_{12}(-\Delta T/T^2) \quad \ldots (1)$$

$$H = L'_{21}(-v\Delta P'/T) + L'_{22}(-\Delta T/T^2) \quad \ldots (2)$$

where J_M, H, $\Delta P'$ and ΔT, respectively stand for mass flow of matter, thermal flow of energy (commonly known as heat flow), the observed solvodynamic pressure difference and temperature difference respectively, acting as the driving forces across a membrane. T is the mean temperature of the two compartments I and II, in the Kelvin scale, v is the specific volume of the fluid concerned and L'^S signify the rate coefficients[10,12]. At a constant mean temperature, T, the above equations may be simplified as

$$J_M = L_{11}(\Delta P') + L_{12}(\Delta T) \quad \ldots (3)$$

$$H = L_{21}(\Delta P') + L_{22}(\Delta T) \quad \ldots (4)$$

where $L_{12}(= -L'_{12}/T^2)$ is known as thermo-osmotic permeability of the permeant at the mean temperature T due to the coupling effect.

Classical theory relates L_{11} and L_{22} to the physical parameters of the system through Poiseuille's and Fourier's equations respectively as given under :

$$L_{11} = n\pi r^4 \rho / 8\eta l \quad \ldots (5)$$

$$L_{22} = K.n\pi r^2/l = K.A/l \quad \ldots (6)$$

in which ρ, n, η, r, l and K represent the density of the permeant at the mean temperature T, no. of capillaries available for permeation of the fluid

* Submitted at the Convention of Chemist held at Waltair in Dec., 1978. (Ref. Abs., Physical Chemistry Section, page no. 5).
** Deoghar College, Deoghar.
† Markoffian system explained at the end.

through the membrane in question, the viscosity of the fluid at temperature T, the average radius[1], the average length[1] of the membrane capillaries and the heat conductivity coefficient respectively. A is the effective cross-sectional area of the membrane. Since K remains constant for an appreciable width of ΔT, L_{22} also behaves similarly at any fixed mean temperature.

In transport processes coupling leads to a decrease in straight coefficients[1,14,15] when restrictions are imposed on fluxes. Thus in thermo-osmosis we obtain equation (8) through equation (7) in association with equation (3) i.e.,

$$(\Delta T)_{H=0} = (-L_{21}/L_{22})\Delta P' \quad \ldots (7)$$

$$(J_M)_{H=0} = L_{11}(1 - L_{12}L_{21}/L_{11}L_{22})\Delta P' \quad \ldots (8)$$

Likewise, we also obtain equation (10) through equation (9) in combination with equation (4)

$$(\Delta P')_{J_M=0} = (-L_{12}/L_{11})\Delta T \quad \ldots (9)$$

$$(H)_{J_M=0} = L_{22}(1 - L_{21}L_{12}/L_{11}L_{22})\Delta T \quad \ldots (10)$$

The quantities in the first parenthesis in the r.h.s. of equation (8) and (10) are the same, positive and less than unity. This is in conformity with the earlier observations[1,14,15].

The absence of either the matter flux or the thermal energy flux in thermo-osmosis is due to a nullifying effect for the generation of the flux of a particular kind by that due to the other because of the thermodynamic equivalence between the two[1]. Thus in thermo-osmosis where the system comprises of two compartments I and II, maintained at two different but constant temperatures, T_1 and T_2, ($T_2 > T_1$) respectively and apparently there is no flow of thermal energy from compartment II to compartment I although the flow of matter continues, it may be argued that the accompanying thermal energy of the outgoing matter from compartment II to compartment I is just counterbalanced by a reverse process of operation i.e. the thermo-mechanical effect, ΔT_{tme} (subscript tme stands for the abbreviation "thermo-mechanical effect"[10] or mechano-caloric effect[10]), so that

$$\overrightarrow{\Delta T_{tme}} = \Delta T = \frac{\overleftarrow{L_{21}}}{L_{22}}\Delta P' \quad \ldots (11)$$

and therefore, the experimentally observed value for thermo-osmotic pressure, $\Delta P'$, developed in the system under such a situation, would apparently record a value which would be a little short of the real and net effective value operative in the system. Hence a part of the real thermo-osmotic pressure which is due to be observed in compartment I, would thus be deemed to be consumed for restraining the temperature rise in it because of the associated thermal energy of the fluid entering in it from compartment II on account of the thermo-osmotic phenomenon. The actual and correct value of the real and net effective thermo-osmotic pressure, ΔP, may therefore, be supposed to be given by a quantity which incorporates the equivalent additive correction factor given by $K_1 \Delta T$ (where $K_1 = S\,\Delta T$ and S is the specific heat of the fluid at the mean temperature, T) in the observed value of $\Delta P'$ for it. Thus

$$\Delta P = \Delta P' + K_1 \Delta T \quad \ldots (12)$$

One can arrive at the above conclusion from other considerations also. We will discuss this aspect a little later.

Poiseuillean flow of a fluid[16,17] (liquid or gas) through a composite membrane consisting of n capillaries gives the following expression[1,18] for the net effective pressure in terms of the rate solvo-dynamic permeation, J_M, as

$$\Delta P = (8\eta l/n\pi r^4 \rho)J_M + (1/n^2\pi^2 r^4 \rho^2)J_M^2 \quad \ldots (13)$$

where every symbol has its usual significance[1]. J_M for the non-linear range is expressed[1] as

$$J_M = \frac{n\pi r^4 \rho}{8\eta l}\Delta P\left(1 + \frac{r^4}{8^2\eta^2 l^2}\Delta P\right)^{-1}$$

$$= \frac{n\pi r^4 \rho}{8\eta l}\Delta P - \frac{n\pi r^8 \rho}{8^3\eta^3 l^3}\Delta P^2 + \frac{n\pi r^{12}\rho}{8^5\eta^5 l^5}\Delta P^3 \quad \ldots (14)$$

Equation (14), however, takes a little different appearance when the transport of a compressed gas is considered in vacuum or against a constant but negligible pressure through the capillaries under the condition such that $\lambda << r$, λ being the mean free path of the gas molecules at temperature T. The boundary condition, i.e., $\vec{u}$ (velocity of gas in any desired direction) at r, under such a situation is affected and a slip of the first molecular layer of the fluid at r of the capillary occurs[17,19]. This situation presents the transition from Poiseuille's flow to Knudsen flow (where J_M is dependent[17,19] on r^3).

[The slip flow expression differs from the true molecular flow (Knudsen flow) by a factor $3\pi/16$. No quantitative kinetic theory treatment of the flow in the transition region ($\lambda \approx r$) exists at present.] J_M under such condition also may, conveniently, be described by an expression in terms of the power series of ΔP. According to Present[19]

$$J_M = \frac{n\pi r^4}{8\eta R'Tl}\cdot\frac{(\Delta P)^2}{2} + \frac{n\pi r^3}{\bar{v}l}\Delta P \quad \ldots 14(a)$$

The average pressure, $\bar{P}$, under the above given condition may be approximately taken as equal to $\Delta P/2$. We will call this system as system 'B' while that of the general i.e., the previous one, as system 'A'. Rearrangement of equation 14(a) leads to

$$\Delta P = \frac{l\bar{v}}{n\pi r^3}\left(1+\frac{r\bar{v}}{16\eta R'T}\Delta P\right)^{-1}. J_M$$

$$= \frac{l\bar{v}}{n\pi r^3}\left(1-\frac{r\bar{v}}{16\eta R'T}\cdot\Delta P\right) J_M \qquad \ldots\ 14(b)$$

wherefrom we obtain

$$J_M = \frac{n\pi r^3}{l\bar{v}}\cdot \Delta P\left(1-\frac{r\bar{v}}{16\eta R'T}\cdot\Delta P\right)^{-1}$$

$$= \frac{n\pi r^3}{l\bar{v}}\Delta P + \frac{n\pi r^4}{16\eta R'Tl}\Delta P^2 + \frac{n\pi r^5\bar{v}}{16^2\eta^2R'^2T^2l}\Delta P^3 + \ldots \qquad \ldots\ 14(c)$$

In the above expressions, $R'(=R/M$, R and M being the molar gas constant and the molecular weight of the gas respectively) is the gas constant per gram of the gas, and $\bar{v}$*$[=(8KT/\pi m)^{1/2}]$ stands for the mean speed of the molecules at the mean temperature, T. It may be noted that L_{11} for J_M in the present situation becomes dependent[19] on r^3 in this slip flow region as against r^4 in the general Poiseullean equation[17,19].

Remembering that the effective thermo-osmotic pressure, ΔP, is governed by equation (12) for a fluid permeation, the correct expression for J_M, in terms of the power series of its driving force, $(\Delta P'+K_1\Delta T)$, viz. the observed thermo-osmotic pressure, and the temperature difference of the system, is given under.

$$J_M = \frac{n\pi r^4\rho}{8\eta l}(\Delta P'+K_1\Delta T) - \frac{n\pi r^8\rho}{8^2\eta^2l^2}(\Delta P'+K_1\Delta T)^2 + \frac{n\pi r^{12}\rho}{8^3\eta^3l^3}(\Delta P'+K_1\Delta T)^3 \qquad \ldots\ (15)$$

which for the flow of a compressed gas against negligible pressure or in vacuum takes the form,

$$J_M = \frac{n\pi r^3}{l\bar{v}}(\Delta P'+K_1\Delta T) + \frac{n\pi r^4}{16\eta R'Tl}(\Delta P'+K_1\Delta T)^2 + \frac{n\pi r^5\bar{v}}{16^2\eta^2R'^2T^2l}(\Delta P'+K_1\Delta T)^3 + \qquad \ldots\ 15(a)$$

Considering now the transfer of thermal energy in the system we find that the total flow of heat energy from compartment II at T_2 to compartment I at T_1 may be supposed to be given by a sum of two factors arising out of two separate contributions : (a) that due to convection on account of thermo-osmosis of the fluid from compartment II at T_2 to compartment I at $T_1(T_2>T_1)$ i.e. $J_1S\Delta T$, where $S(=C_v$ in the case of a compressed gas) is the specific heat of the fluid at the mean temperature T and (b) that due to conduction i.e. J_2 given by the quantity $K.n\pi r^2/l$. The net flow of heat energy in the system from compartment at T_2 to that at T_1 in the linear range, therefore, may be written as,

$$H = J_1S\Delta T + J_2(=K.n\pi r^2\Delta T/l) \qquad \ldots\ (16)$$

Before attempting to obtain a non-linear expression for heat flow we would like to add that the two fluxes, viz. the mass flow and the heat flow, in the present context may, conveniently, be described by the equalities,

$$J_M = J_1 + OJ_2 \qquad \ldots\ (17)$$

$$H = K_1J_1 + J_2 \qquad \ldots\ (18)$$

In the above equations J_1 is the mass flow due to the observed thermo-osmotic pressure i.e., $\Delta P'$ and J_2 is the heat flow due to conduction. The first term in the r.h.s. of equation (18) refers to the flow of thermal energy by convection.

The entropy production, ϕ, for the system, described by

$$\phi = \Sigma J_iX_i = J\Delta P' + H\Delta T \qquad \ldots\ (19)$$

may, in the light of equations (17) and (18), be written as

$$\phi = J_1\Delta P' + (K_1J_1+J_2)\Delta T$$

$$= J_1\Delta P' + K_1J_1\Delta T + J_2\Delta T$$

$$= J_1(\Delta P'+K_1\Delta T) + J_2\Delta T \qquad \ldots\ (20)$$

In equation (20) we find the new force for solvodynamic permeation to be given by $(\Delta P'+K_1\Delta T)$ i.e., the net total effective pressure as envisaged in our equation (12).

To obtain the non-linear range, in terms of L_i's Taylor type expansion in power series of ΔT and $\Delta P'$ we replace J_1 in the 1st term of the right-hand side of equation (16) by its expression in the power series of $\Delta P'$ and ΔT given by equations (15) and 15(a) for thermo-osmotic flow of a fluid, respectively, for system A and system B. The expression for H, in terms of L's whose meaning is given by the corresponding coefficients of the equivalent

* The Maxwell-Boltzman equilibrium distribution function $f^{(0)}$ has been used for the derivation of the above equation, since it is sufficiently valid approximation for near equilibrium situations to which our system belongs. The number density of molecules is constant irrespective of the type of distribution[9(a),20]

$$\int fcdc = \int f^0cdc$$

where f is the true distribution function and c is the velocity. Hence the average velocity of molecules is the same as in equilibrium provided the local temperature is not altered. As in earlier approaches of this kind,[1,3,9(a)] the domain of the validity of Gibb's equation has been assumed to hold in the present case also. This is also in conformity with the ideas advanced by Prigogine[21].

powers of $(\Delta P'+K_1\Delta T)$ in equations (15) and 15(a), thus becomes[8]

$$H=K_1\Big[L_{11}(\Delta P'+K_1\Delta T)+\frac{1}{2!}L_{111}(\Delta P'+K_1\Delta T)^2+\frac{1}{3!}L_{1111}(\Delta P'+K_1\Delta T)^3+\cdots\cdots\Big]+L_{22}\Delta T$$

wherefrom on simplification and rearrangement we obtain,

$$\begin{aligned}H=&K_1L_{11}\Delta P'+(K_1^2L_{11}+L_{22})\Delta T\\&+\frac{1}{2!}K_1L_{111}(\Delta P')^2+K_1^2L_{111}(\Delta P')(\Delta T)\\&+\frac{1}{2!}K_1^3L_{111}(\Delta T)^2+\frac{1}{3!}K_1L_{1111}(\Delta P')^3\\&+\frac{1}{3!}.3.L_{1111}(\Delta P')^2\Delta TK_1^2\\&+\frac{1}{3!}.3.L_{1111}\Delta P'(\Delta T)^2K_1^3\\&+\frac{1}{3!}L_{1111}K_1^4(\Delta T)^3+\end{aligned}\qquad\ldots\quad(21)$$

Similarly from equations (14) and 14(c) we get[8] J_M as

$$\begin{aligned}J_M=&J_1[\text{cf. eqn. (17)}].\\=&L_{11}(\Delta P'+K_1\Delta T)+\frac{1}{2!}L_{111}(\Delta P'+K_1\Delta T)^2\\&+\frac{1}{3!}L_{1111}(\Delta P'+K_1\Delta T)^3+\cdots\cdots\end{aligned}$$

Proper arrangement of which in terms of $\Delta P'$ and ΔT gives,

$$\begin{aligned}J_M=&L_{11}\Delta P'+K_1L_{11}\Delta T\\&+\frac{1}{2!}L_{111}(\Delta P')^2+L_{111}K_1\Delta P'\Delta T\\&+\frac{1}{2!}L_{111}K_1^2(\Delta T)^2+\frac{1}{3!}L_{1111}(\Delta P')^3\\&+\frac{1}{3!}.3.L_{1111}(\Delta P')^2\Delta TK_1\\&+\frac{1}{3!}.3.L_{1111}\Delta P'(\Delta T)^2K_1^2\\&+\frac{1}{3!}L_{1111}(\Delta T)^3K_1^3+\end{aligned}\qquad\ldots\quad(22)$$

If subscripts 1 and 2 associated with L'^{s} are now recognised for the indication of matter flow and thermal energy (heat) flow respectively, as has been done in equations (3) and (4) earlier, then from equations (21) and (22) we obtain the followin equalities, akin to those of electro-kinetics, with parametric equations in terms of L^{S} as used in the steady state thermodynamics[9,10].

System 'A'

$$\begin{aligned}L_{21}&=K_1L_{11}=K_1.n\pi r^4\rho/8\eta l=L_{12}\\2L_{211}&=K_1L_{111}=K_1.2\,!\;n\pi r^8\rho/8^2\eta^2l^2=L_{112}\\L_{212}&=K_1^2L_{111}=K_1^2.2\,!\;n\pi r^8\rho/8^2\eta^2l^2=2L_{122}\\3L_{2111}&=\tfrac{1}{2}K_1L_{1111}=\tfrac{1}{2}.K_1.3\,!\;n\pi r^{12}\rho/8^3\eta^3l^3\\&=L_{1112}\\L_{2122}&=\tfrac{1}{2}K_1^2L_{1111}=\tfrac{1}{2}K_1^2.\;3\,!\;n\pi r^{12}\rho/8^3\eta^3l^3\\&=3L_{1222}\end{aligned}\qquad\ldots\quad(23)$$

System 'B'

$$\begin{aligned}L_{21}&=K_1L_{11}=K_1.n\pi r^3/l\bar{v}=L_{12}\\2L_{211}&=K_1L_{111}=K_1.2\,!\;n\pi r^4/16\eta R'Tl={}_{112}\\L_{212}&=K_1^2L_{111}=K_1^2.2\,!\;n\pi r^4/16\eta R'Tl=2L_{122}\\3L_{2111}&=\tfrac{1}{2}K_1L_{1111}=\tfrac{1}{2}K_1.3\,!\;n\pi r^5\bar{v}/16^2\eta^2R'^2T^2l\\&=L_{1112}\\L_{2122}&=\tfrac{1}{2}K_1^2L_{1111}=\tfrac{1}{2}K_1^2.3\,!\;n\pi r^5\bar{v}/16^2\eta^2R'^2T^2l\\&=3L_{1222}\end{aligned}\qquad\ldots\quad 23(a)$$

In observing the above symmetries it has to be noted that the above equalities are obtained through the association of L_{11}, L_{111} and L_{1111} etc. with K_1 ($=S\Delta T$, S being the specific heat of a liquid at the mean temperature T, in case of a gas it is taken as Cv) which we have assumed to be a constand quantity. But K_1 is constant only when ΔT is kept unaltered at the constant mean temperature T. The temperature difference ΔT, between the two chambers under consideration may, however, be conveniently varied without in any way affecting the fixed mean temperature T. It is, therefore, of interest to investigate the impact of the variation of ΔT (between the two chambers, keeping the mean temperature, T unaltered) on the L^{s} and the equalities. For this K_1 ($=S\Delta T$ or $Cv\,\Delta T$) of equations (21) and (22) is replaced by $S.\Delta T$. This leads to equations (24) and (25). The factor ΔT in $K_1(=S\Delta T)$, which was dormant and non-operative as a force in equations (21) and (22), associates itself with the operative part of the force as ΔT in the system and thereby reshapes equations (21) and (22) as given in equations (24) and (25) respectively.

$$H = SL_{11}(\Delta P')(\Delta T) + S^2L_{11}(\Delta T)^3 + L_{22}\Delta T + \frac{1}{2!}L_{111}S(\Delta P')^2(\Delta T) + S^2L_{111}(\Delta P')(\Delta T)^3 + \frac{1}{2!}S^3L_{111}(\Delta T)^5 + \frac{1}{3!}L_{1111}S(\Delta P')^3(\Delta T) + \frac{1}{3!}3L_{1111}S^2(\Delta P')^2(\Delta T)^3 + \frac{1}{3!}3L_{1111}S^3(\Delta P')(\Delta T)^5 + \frac{1}{3!}L_{1111}S^4(\Delta T)^7 + \cdots \quad \ldots (24)$$

$$J_M = L_{11}(\Delta P') + L_{11}S(\Delta T)^2 + \frac{1}{2!}L_{111}(\Delta P')^2 + L_{111}S(\Delta P')(\Delta T)^2 + \frac{1}{2!}L_{111}S^2(\Delta T)^4 + \frac{1}{3!}L_{1111}(\Delta P')^3 + \frac{1}{3!}3L_{1111}S(\Delta P')^2(\Delta T)^2 + \frac{1}{3!}3L_{1111}S^2\,\Delta P'(\Delta T)^4 + \frac{1}{3!}L_{1111}S^3(\Delta T)^6 + \cdots \quad \ldots (25)$$

Equations (24) and (25) may be rearranged in a proper sequence of ΔP and ΔT which, when rewritten in the conventional $L'_1{}^s$ Taylor type expansion form, appear as given in equations (26) and (27).

$$H = L^*_{212}\Delta P'\Delta T + L^*_{222}(\Delta T)^3 + L^*_{22}\Delta T + \frac{1}{2!}L^*_{2112}(\Delta P')^2\Delta T + L^*_{21222}\Delta P'(\Delta T)^3 + \frac{1}{2!}L^*_{222222}(\Delta T)^5 + \frac{1}{3!}L^*_{21112}(\Delta P')^3\Delta T + \frac{1}{3!}L^*_{211222}(\Delta P')^2(\Delta T)^3 + \frac{1}{3!}L^*_{2122222}\Delta P'(\Delta T)^5 + \frac{1}{3!}L_{22222222}(\Delta T)^7 + \cdots \quad \ldots (26)$$

$$J_M = L^*_{11}\Delta P' + L^*_{122}(\Delta T)^2 + \frac{1}{2!}L^*_{111}(\Delta P')^2 + L^*_{1122}\Delta P'(\Delta T)^2 + \frac{1}{2!}L^*_{12222}(\Delta T)^4 + \frac{1}{3!}L^*_{1111}(\Delta P')^3 + \frac{1}{3!}L^*_{11122}(\Delta P')^2\Delta T^2 + \frac{1}{3!}L^*_{112222}\Delta P'(\Delta T)^4 + \frac{1}{3!}L^*_{1222222}(\Delta T)^6 + \cdots \quad \ldots (27)$$

Adopting now the same procedure, as observed earlier, for examining the obeyance of the higher order symmetries one again obtains the equalities shown in (28) and 28(a) through the same set of parameters. Thus we have for

System 'A'

$$L^*_{212} = S.L_{11} = S.n\pi r^4\rho/8\eta l = L^*_{122}$$

$$2L^*_{2112} = S.L_{111} = S.2!\ n\pi r^6\rho/8^2\eta^2l^2 = L^*_{1122}$$

$$L^*_{21222} = S^2.L_{111} = S^2.2!\ n\pi r^6\rho/8^2\eta^2l^2 = 2L^*_{12222}$$

$$3L^*_{21112} = \tfrac{1}{2}S.L_{1111} = \tfrac{1}{2}S.3!\ n\pi r^{12}\rho/8^3\eta^3l^3 = L^*_{11122}$$

$$L^*_{2122222} = \tfrac{1}{2}S^3.L_{1111} = \tfrac{1}{2}S^3.3!\ n\pi r^{12}\rho/8^3\eta^3l^3 = 3L^*_{1222222} \quad \ldots (28)$$

System 'B'

$$L^*_{212} = C_v(=S).L_{11} = C_v.n\pi r^3/l\bar{v} = L^*_{122}$$

$$2L^*_{2112} = C_v.L_{111} = C_v.2!\ n\pi r^4/16\eta R'Tl = L^*_{1122}$$

$$L^*_{21222} = C_v^2.L_{111} = C_v^2.2!\ n\pi r^4/16\eta R'Tl = 2L^*_{12222}$$

$$3L^*_{21112} = \tfrac{1}{2}C_v.L_{1111} = \tfrac{1}{2}C_v.3!\ n\pi r^5\bar{v}/16^2\eta^2R'^2T^2l = L^*_{11122}$$

$$L^*_{2122222} = \tfrac{1}{2}C_v^3.L_{1111} = \tfrac{1}{2}C_v^3.3!\ n\pi r^5\bar{v}/16^2\eta^2R'^2T^2l = 3L^*_{1222222} \quad \ldots 28(a)$$

As pointed out earlier the values of the L'^s with identical supercripts in the equalities shown in equation (23) differ in set and magnitude of the parameters from that shown in equation (28). Similar is the case with the equalities shown in equations 23(a) and 28(a) also. The difference as will be observed, is very symmetrical and is accounted for the fact discussed in earlier pages. If we look into their interrelationship we find that the equalities of equations (23) and 23(a) i.e., $L_{21} = L_{12}$, $2L_{211} = L_{112}$ and $L_{212} = 2L_{122}$ etc. become correspondingly, equal to the equalities, $L^*_{212} = L^*_{122}$, $2L^*_{2112} = L^*_{1122}$ and $L^*_{21222} = 2L^*_{12222}$ etc. of equations (28) and 28(a) respectively with the same and identical parametric values on account of the fact discussed subsequently after equation 23(a).

Acknowledgement

One of us (S.P.J.) is thankful to Dr. Md. Zakaria for active help and participations in the preparation of this paper.

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Note : For Markoffian system, the fluxes at a given instant depend only on the value of affinity at that instant, for example a pure resistor, whereas a circuit with capacitance and inductance in which the fluxes may depend upon the values of the affinites at previous time as well as at that instant, is a non-Markoffian system.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1098-1100

Effect of Independent Additions of Inorganic Salts of Nitrogen, Phosphorus and Sulphur on Sulphur Mineralisation of the Native Organic Matter in Soil

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Manuscript received 2 July 1980, accepted 25 August 1980

Laboratory incubation studies were conducted on the effect of independent additions of $Ca(NO_3)_2$, KH_2PO_4 and K_2SO_4 on the mineralisation of sulphur in two soils. Sulphur mineralisation was found to be related to the initial sulphate sulphur and organic sulphur content of the soils. Addition of $Ca(NO_3)_2$ widens the N : S ratio and resulted immobilisation of sulphur in soil. Depending upon the initial sulphate sulphur content of the soil, addition of KH_2PO_4 or K_2SO_4 either stimulates or inhibits the net mineralisation of sulphur contained in the native organic matter in soil.

RESULTS of his experiment led Barrow[1] to suggest that mineralisation of sulphur depends on the concentration of other elements. However, there are few reports on the effect of varying supply of other nutrient ions on the mineralisation or immobilisation of sulphur. In another study Barrow[2] observed considerable increase in the extractable sulphate when urea was incubated with a soil. Kwalenko and Lowe[3] reported that addition of nitrogen resulted decrease in sulphur mineralisation during 8 week period of incubation.

Sulphur deficiency in agricultural soils of West Bengal has been increased in recent years due to the decreased use of sulphur containing fertilisers (ammonium sulphate, super phosphate and potassium sulphate) and intensive cropping. Mukhopadhyay and Mukhopadhyay[4] also observed that inorganic sulphate sulphur content of the non-saline soils (0-15 cm) of West Bengal varies from 0.6 ppm to 27.5 ppm. Hence use of sulphur as fertiliser element and studies on the factors influencing its mineralisation are of considerable importance. Using tracer technique Sachdev and Chhabra[5] observed that 68.1% of the added sulphur was present as sulphate sulphur in an alluvial soil even after four months period of incubation under aerobic condition. In view of the above a laboratory incubation was, therefore, conducted to study the independent addition of inorganic salts of nitrogen, phosphorus and sulphur on sulphur mineralisation from the native organic matter in the soil.

Experimental

The study was conducted on two soils (0-15 cm layer samples) collected from Mundabasti in Darjeeling district of the sub-Himalayan Hill region and Chinsurah in Hooghly district of the Gangetic Alluvial region. After collection, the soils were ground to pass through 0.5 mm sieve. Relevant characteristics of the soils are presented in Table 1.

For the laboratory incubation study, 25 g of each of the two soil samples was taken in a glass container and to which the respective treatment materials were separately added and allowed to incubate at laboratory room temperature (30±5°) under 50% of the moisture holding capacity. Loss of moisture due to evaporation was adjusted by addition of water on every alternate day. Separate and duplicate samples for each treatment was maintained for each of the five sampling stages corresponding to 15, 30, 45, 60 and 75 days of incubation.

TABLE 1—PROPERTIES OF THE SOILS

Soil samples collected from	pH (1 : 2.5)	% water holding capacity	% organic carbon	% total nitrogen	% total sulphur	Organic sulphur (ppm)	0.15 % $CaCl_2$ extractable sulphate sulphur (ppm)	N : S
Mundabasti	[illegible]	68	3.14	0.424	0.0219	218.1	0.6	19.3
Chinsurah	8.0	32	0.77	0.071	0.0062	49.7	12.8	11.4

TABLE 2—EFFECT OF INORGANIC SALT OF NITROGEN ADDITION ON SULPHUR MINERALISATION

Soil samples collected from	Levels of N-added (ppm)	S-mineralised (ppm) Incubation periods in days: 15		30		45		60		75	
		A	B	A	B	A	B	A	B	A	B
Mundabasti	200	1.25	− 4.37	0	−2.19	0	−2.81	0	−3.44	0.31	−2.81
	100	1.56	− 3.12	0.16	−2.03	0	−2.81	1.25	−2.19	0.31	−2.81
Chinsurah	200	1.25	−14.37	3.75	−5.63	1.87	−6.57	1.12	−5.75	0.62	−7.19
	100	0.94	−14.68	0	−9.38	0	−8.44	0.16	−6.77	2.19	−5.62

A = Sulphate sulphur content
B = Increase of sulphate sulphur over control.

TABLE 3—EFFECT OF INORGANIC SALT OF PHOSPHORUS ADDITION ON SULPHUR MINERALISATION

Soil samples collected from	Levels of P-added (ppm)	S-mineralised (ppm) Incubation period in days: 15		30		45		60		75	
		A	B	A	B	A	B	A	B	A	B
Mundabasti	200	2.50	−3.12	0.62	−1.57	0.47	−2.34	0.62	−2.82	0.94	−2.18
	100	2.81	−2.81	2.19	0	2.50	−0.31	2.19	−1.25	1.56	−1.56
Chinsurah	200	19.37	3.75	20.00	10.62	12.50	4.06	—	—	9.69	1.88
	100	12.19	−3.43	13.12	3.74	18.12	9.08	10.62	3.75	13.12	5.31

A = Sulphate sulphur content
B = Increase of sulphate sulphur over control.

Besides an untreated control there were six other treatments adopted for the present investigation. Each of the three sources of nitrogen, phosphorus and sulphur were added at two levels corresponding to 200 and 100 ppm for N and P and 40 and 20 ppm with respect to S. Nitrogen in the form $Ca(NO_3)_2$, phosphorus as KH_2PO_4 and sulphur as K_2SO_4 were added.

Sulphate sulphur content in the soil at each stage was extracted with 0.15% calcium chloride solution (Kwalenko and Lowe[3]) and determined by the reduction method of Johnson and Nishita[6]. The effect of added salts of N, P or S on the sulphur mineralisation from the native soil organic matter was calculated by subtracting the value of control from the corresponding treated samples.

Results and Discussion

The two soils used in this study indicated considerable differences in their chemical properties (Table 1). Organic sulphur content of Mundabasti soil was 218.1 ppm whereas, that of Chinsurah soil was 49.7 ppm. But 0.15% $CaCl_2$ extractable sulphate sulphur was found to be much higher in Chinsurah (12.8 ppm) than that in Mundabasti (0.6 ppm) soil.

Inorganic salt of Nitrogen :

Addition of nitrogen as $Ca(NO_3)_2$ caused a decrease in the mineralisation of sulphur from the native soil organic matter over the untreated control. This was observed in both the soils, at both the levels of added nitrogen and at all the five stages of sampling over 75 day period of incubation (Table 2). Since nitrogen and sulphur exist in close relationship in soil organic matter, many workers (Freney and Spencer[7] and Williams[8]) viewed that the mineralisation of sulphur would be similar to that of nitrogen. Hence N : S ratio of the soil may affect the amount of sulphur mineralised in the same way as C : N ratio affect the amount of nitrogen mineralised. Addition of nitrogen increased the N : S ratio in both the soils and hence a decrease in the rate of sulphur mineralisation was noted in the soils. The observed results are in agreement with those of Kwalenko and Lowe[3]. The extent of sulphur immobilisation was more intense in Chinsurah soil than that in Mundabasti soil. Addition of 200 ppm of $Ca(NO_3)_2$ caused the N : S ratio of Chinsurah soil to increase from 11.4 to 14.6, whereas, it increased from 19.3 to 20.2 in Mundabasti soil. This might explain the observed variation between the two soils.

Inorganic salt of Phosphorus :

Inorganic phosphate addition resulted in immobilisation of available sulphate sulphur in Mundabasti soil (Column B of Table 3). Increasing the level of phosphate resulted in higher amount of sulphur immobilisation. These were observed at all the five stages of sampling over the 75 day period of incubation. Whereas, an increase in the amount

TABLE 4—EFFECT OF INORGANIC SALT OF SULPHUR ADDITION ON SULPHUR MINERALISATION

Soil samples collected from	Levels of S-added (ppm)	S-mineralised (ppm) Incubation period in days: 15		30		45		60		75	
		A	B	A	B	A	B	A	B	A	B
Mundabasti	40	4.69	−0.93	1.87	−0.32	2.81	0	2.19	−1.25	2.50	−0.62
	20	5.31	−0.31	1.12	−1.07	1.87	−0.94	0.62	−2.82	1.25	−1.87
Chinsurah	40	25.62	10.00	25.31	15.93	21.25	12.81	16.87	10.00	19.06	11.25
	20	13.75	−1.87	14.06	4.68	12.19	3.75	10.31	3.44	12.81	5.00

A = Sulphate sulphur content
B = Increase of sulphate sulphur over control.

of available sulphate sulphur over the control (mineralisation) was observed under the similar situation in Chinsurah soil. In the first one month period of incubation the said increase was higher at the higher level of phosphorus application (200 ppm). In the subsequent period, however, the higher amount of sulphur mineralisation was recorded at lower level of added phosphorus. The results thus corroborate the findings of Barrow[1] that mineralisation of sulphur depends on the concentration of added phosphorus. The variation in the nature and amount of the native soil organic matter and its sulphate content might explain the opposite trend of results in Mundabasti and Chinsurah soil.

Inorganic salt of Sulphur :

Corresponding changes in available sulphate sulphur content following the addition of inorganic sulphate (K_2SO_4) to the same two soils are presented in Table 4. Results (Column B) reveal that Mundabasti soil immobilise not only the added sulphate but also the amount of available sulphate sulphur which are already present in the soil. After the first 15 day period of incubation, the extent of sulphur immobilisation was found to be higher at lower level of sulphur addition.

On the other hand, although considerable amount of inorganic sulphur was *immobilised in* Chinsurah soil, the extent of sulphur immobilisation at no stage exceeded 75% of the 40 ppm level of application (Column B, Table 4). Much higher amount of the added sulphur was immobilised in the Chinsurah soil at 20 ppm level of application. At the initial stage of incubation (15 day period) an amount of 1.87 ppm of available sulphate sulphur over the 20 ppm of added sulphur was found to be immobilised in the soil. Mineralisation of recently immobilised sulphur was however, noted at the later period of incubation. But the amount mineralised at no stage exceeded 25% of the added amount (20 ppm). Hesse[9] however, observed increased sulphate formation in a forest soil following the addition of sulphur as $CaSO_4$ over 30 day period of incubation. On the other hand, results of laboratory incubation studies of Barrow[1] indicated that with low levels of sulphur supply there was a tendency of mineralisation of sulphate and after the initial lag phase in microbial development was over mineralisation of sulphur occurred in the soil.

Acknowledgement

One of the authors (P.M.) is grateful to the Indian Council of Agricultural Research for award of Senior Research Fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1101-1105

Studies on Hydrated Stannic Oxide : Part V : Selective Recovery of Phosphate from Basic Slag

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Manuscript received 7 April 1979, revised 1 July 1980, accepted 7 August 1980

K_d values of phosphate, Al^{3+}, Fe^{3+}, Mn^{2+}, Ca^{2+} and Mg^{2+} were studied on hydrated stannic oxide. Based on this a process of recovery of phosphate from basic slags of Indian Steel Plants is suggested with a recovery of over 95%.

HYDRATED stannic oxide acts as a cation as well as anion exchanger[1,2]. Its anion exchange properties have been investigated extensively in our laboratory[2-4]. During the study it was observed that phosphate has high K_d-value at pH 2. This was made use of for a selective recovery of phosphate from basic slags of Indian Steel Plants.

Experimental

Reagents : All the reagents were of analytical grade.

Apparatus : ELICO pH meter model LI-10 (India) was used for pH measurement.

Spectromom-202 (Hungary) was used for spectrophotometric measurements.

Anion exchange column (i.d. 1.2 cm, length-3.0 cm) was used for column operation.

Preparation of hydrated stannic oxide (batch 2) :

As reported earlier[3]. It was then dried at 300° for one hour before use. The exchanger is insoluble in 1(M) NaOH and 2(M) $HClO_4$.

Results and Discussion

Composition of Basic Slags :

The composition in percentage of basic slags of different Indian Steel Plants were determined[5-7] : Bokaro Basic Slag, CaO (42.25), MgO(4.62), FeO (16.86), MnO(4.50), Al_2O_3(6.42), P_2O_5(2.24), SiO_2 (22.35) ; Burnpur Basic Slag, CaO(41.90), MgO (6.97), FeO(15.75), MnO(5.45), Al_2O_3(7.25), P_2O_5 (5.41), SiO_2(16.70) ; B.A.S. Basic Slag (31a)† CaO (45.00), MgO(7.44), FeO(5.65), MnO(5.01), Al_2O_3 (1.6), P_2O_5(13.3), SiO_2(14.6).

Ion-Exchange capacity measurement :

The ion-exchange capacity of hydrated stannic oxide (OH^- form) was estimated by batch operation[8]. One gram of hydrated stannic oxide was equilibrated with 100 ml of 1.9(M) $NaNO_3$ in 0.1M HNO_3 solution for 40 hours at room temperature. The amount of acid neutralised was estimated with standard sodium hydroxide solution. The anion exchange capacity was found to be 1.32 meq. (NO_3^-)/gm of hydrated stannic oxide.

Distribution co-efficient (K_d) measurement :

The distribution co-efficient (K_d-values) of phosphate, Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+} and Mn^{2+} at pH 2 (initial) were determined by equilibrating 100 ml of metal ions/phosphate solutions for 40 hours at room temperature with one gram of hydrated stannic oxide (OH^- form). The metal ions and phosphate concentration were kept at 4.5×10^{-4}(M). The metal ions present in the solution phase before and after shaking were estimated with standard disodium salt of EDTA[8] solution and phosphate present in the solution phase before and after shaking was estimated spectrophotometrically[9]. The K_d-values were calculated as before[3] given in Table 1.

TABLE 1—DISTRIBUTION CO-EFFICIENTS OF THE IONS ON HYDRATED STANNIC OXIDE AT (80 ± 2°C)

Anions/Cations	K_d-value
Phosphate	Total adsorption
Al^{3+}	0.2
Fe^{3+}	82.9
Mn^{2+}	1.1
Ca^{2+}	0.2
Mg^{2+}	0.9

Phosphate uptake by the different forms of exchanger :

Different forms (NO_3^-, Cl^-, SO_4^{2-}) of the

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† Data supplied by Bureau of Analysed Sample Ltd.

exchanger were prepared by shaking the exchanger (OH^- form) with 2(*M*) of corresponding sodium salt in 0.1(*M*) corresponding acid, then washed with deionised water and dried. Phosphate uptake by the different forms of exchanger at *p*H 2 (initial) was determined by following method : 0.5 g of different forms of exchanger were shaken with 100 ml of 5×10^{-3}(*M*) phosphate solution in different bottles for 40 hours at room temperature. The phosphate in solution phase before and after shaking was determined spectrophotometrically[6]. The phosphate uptake has been calculated by the difference and tabulated in Table 2. Nitrate and chloride ions interfered during estimation of phosphate[6] and manganese[7] respectively. Hence sulphate form of exchanger was used in the latter part of the work. It is evident from the results in Table 2, that phosphate uptake by the exchanger is highest (15.1 mg/0.5 g exchanger) when the exchanger is in the OH^- form whereas phosphate uptake is least (12.2 mg/0.5 g exchanger) when the exchanger is in the NO_3^- form.

TABLE 2—PHOSPHATE UPTAKE BY THE DIFFERENT FORM OF HYDRATED STANNIC OXIDE AT *p*H 2 (INITIAL)

Form of exchanger	Phosphate uptake (mg/ 0.5 g exchanger)
OH^- form	15.1
NO_3^- form	12.2
Cl^- form	13.8
SO_4^{2-} form	13.2

Interference study :

The interference due to NO_3^-, Cl^-, SO_4^{2-}, Fe^{3+}, Al^{3+}, Mn^{2+}, Ca^{2+} and Mg^{2+} on phosphate uptake by hydrated stannic oxide (OH^- form) at *p*H 2 (initial) were studied by equilibration as before. The results are presented graphically (Figs. 1 and 2).

It is evident from the results that SO_4^{2-} ion (bivalent) competes more strongly with the PO_4^{3-} ion than Cl^- or NO_3^- ion. At low concentration of SO_4^{2-} ion, PO_4^{3-} ion is more selective than SO_4^{2-} ion by the exchanger under identical condition [$K_{d_{SO_4^{2-}}} = 290$ and $K_{d_{PO_4^{3-}}}$ = Total adsorption].

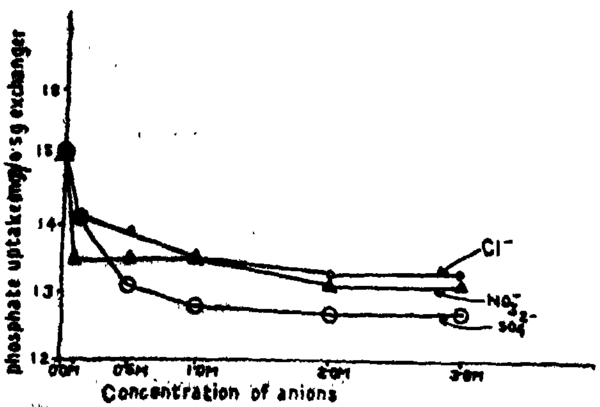


Fig. 1. Interference of anions on phosphate uptake by hydrated tin dioxide

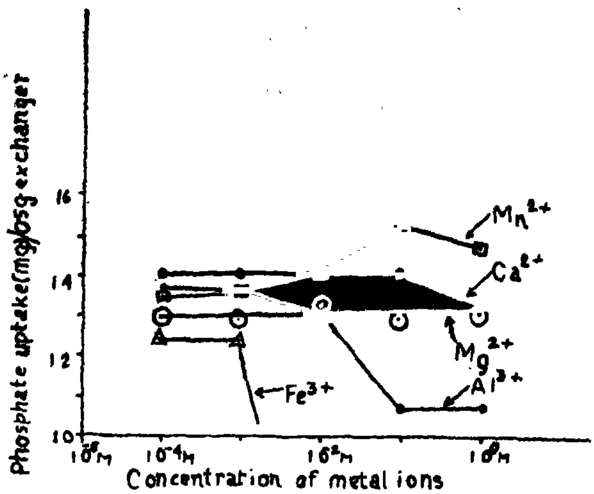


Fig. 2. Interference of metal ions on phosphate uptake by hydrated tin dioxide.

The interference on phosphate uptake by the exchanger is slight due to presence of 10^{-4}(*M*) any foreign cations in the solutions. When the concentration of Fe^{3+} is higher than 10^{-3}(*M*) in solution phase, it affects the phosphate uptake considerably. However, this interference due to Fe^{3+} ion was removed by dilution. It was observed that when 100 ml of the mixture containing 5×10^{-3}(*M*) PO_4^{3-} and 10^{-3}(*M*) Fe^{3+} was diluted to 300 ml and the mixture was shaken with 0.5 g of the exchanger, the interference was considerably minimised. For large scale industrial application the amount of iron in the slag can be reduced by initial electromagnetic separation.

Column elution study :

Breakthrough capacity is more important for column operation. The breakthrough capacity of hydrated stannic oxide column was determined as follows : the column. (i.d. 1.2 cm, length 3.0 cm) was prepared with 5 gms of hydrated stannic oxide (OH^- form) of particle size 100-200 mesh. It was washed with dilute H_2SO_4 of appropriate strength before use. *p*H of the phosphate solutions (0.88 mg/ml) were adjusted with dilute H_2SO_4. The phosphate solutions were then passed through the column with a flow rate 0.8-1.0 ml/minute. It was observed that leakage of phosphate started at *p*H 2-4 after 10 ml of effluent which indicated that maximum 8.8 mg phosphate is adsorbed under that condition.

Elution studies of phosphate were carried out with 1.0(*M*) $(NH_4)_2SO_4$ in 1.0(*M*) H_2SO_4, 2.0(*M*)

$(NH_4)_2SO_4$ in 1.0(*M*) H_2SO_4, 0.1(*M*) NH_4OH, 0.5(*M*) NH_4OH, 0.1(*M*) NaOH, 0.5(*M*) NaOH, 1.0(*M*) NaOH and 2.0(*M*) H_2SO_4. Quantitative elution of phosphate was obtained either with 1.0(*M*) NaOH or 2.0(*M*) H_2SO_4. Elution constant (E=0.2285) and bed distribution co-efficient $(D=\frac{1}{E}=4.376)$ for 1.0(*M*) NaOH eluant was calculated as usual[10].

Individual solutions of Al^{3+}, Fe^{3+}, Mn^{2+}, Ca^{2+}, Mg^{2+} and PO_4^{3-} at *p*H 2 (initial) were passed through the exchanger column. Fe^{3+} was partly adsorbed and then selectively eluted either with 35 ml of 2(*M*) $HClO_4$ or with 25 ml of 0.72(*M*) H_2SO_4 while phosphate remained adsorbed strongly by the hydrated stannic oxide. The phosphate was eluted quantitatively with 250 ml of aqueous 1.0(*M*) NaOH. The rate of elution was kept at 5-6 drops/minute.

The selective separation of phosphate from binary mixture with Al^{3+}, Fe^{3+}, Mn^{2+}, Ca^{2+} and Mg^{2+} (containing ~0.5 mg phosphate and ~0.5 mg metal ion in solution) have been achieved initially. Only in the case of Fe^{3+}-PO_4^{3-} mixture, Fe^{3+} was selectively eluted as above while phosphate remained adsorbed strongly by the exchanger.

On the basis of the above experimental results, a synthetic mixture of basic slag, similar in composition to Burnpur basic slag containing phosphate 0.1 mg/ml, was prepared. The *p*H of the solution was kept nearly at 1.7 (initial).

An aliquot of synthetic basic slag solution was added at the top of the exchanger column (sulphate form) and the effluent was collected. The column was washed with 35 ml 2(*M*) $HClO_4$ followed by 20 ml distilled water. The total effluent was tested for phosphate and found absent. The mixed effluent in duplicate runs was analysed and found that all metal ions including Fe^{3+} were present quantitatively. Adsorbed phosphate was then eluted with 250 ml of 1 (*M*) NaOH solution. The rate of elution was kept at 5-6 drops/minute. Phosphate was estimated spectrophotometrically[9].

The above experiment was repeated with the Burnpur basic slag, B.A.S. basic slag (31a) and Bokaro basic slag. The slag solutions except Bokaro slag were prepared in such a way that the concentration of phosphate in solution became 0.1 mg/ml. In the case of Bokaro slag solution, the phosphate concentration was adjusted at 0.05 mg/ml in order to lower down the interference of Fe^{3+} on the uptake of phosphate by hydrated stannic oxide. The *p*H of all the solutions were kept at 1.7 (initial). The phosphate recovery was fairly satisfactory and reproducible. The results are tabulated in Table 3.

TABLE 3 RECOVERY OF PHOSPHATE FROM BASIC SLAG

Slag's solution *p*H 1.7	PO_4^{3-} taken (mg)	PO_4^{3-} recovered (mg)	% of recovery
Synthetic	4.5	4.48	99.5
Burnpur	4.5	4.46	99.1
B.A.S. (31a)	5.0	4.9	98.00
Bokaro	3.2	3.12	97.5

Acknowledgement

The authors are thankful to University Grants Commission (India) for a fellowship to one of the authors (U.C.G.), to Prof. A. K. De, Department of Chemistry, Visva-Bharati, for constant encouragement and to the managements of different Indian Steel Plants who have supplied the samples of basic slags.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1104-1105

Reaction of Arylidenecyanoacetamides with *p*-Tolyltetrachlorophosphorane

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Manuscript received 7 November 1979, revised 12 June 1980, accepted 7 August 1980

Arylidenecyanoacetamides react with p-tolyltetrachlorophosphorane in refluxing carbon tetrachloride to give N-(arylidenecyanoacetyl)-p-tolylphosphonimidic dichlorides. The structural assignments of the products were based on IR and chemical reactions.

IN previous publications[1,2], we have described the reaction of arylidenecyanoacetamides(I) with phosphorus pentachloride and phenyltetrachlorophosphorane. In this work, the reaction of compounds(I) with *p*-tolyltetrachlorophosphorane is investigated.

Thus, when compounds(I) were refluxed with *p*-tolyltetrachlorophosphorane(II) in carbon tetrachloride, until the evolution of hydrogen chloride gas ceased (ca., 1.5 hr), they gave N-(arylidenecyanoacetyl)-*p*-tolylphosphonimidic dichlorides(III).

$$\underset{\text{(I)}}{ArCH{=}C(CN){-}CONH_2} + \underset{\text{(II)}}{RPCl_4} \rightarrow 2\,HCl + \underset{\text{(III)}}{ArCH{=}C(CN){-}CON{=}PRCl_2}$$

The reaction of dichlorides(III) with aniline as well as with anhydrous formic acid yielded the corresponding dianilides(IV) and N-(arylidenecyanoacetyl)-*p*-tolylphosphonamidic acid(V) respectively.

$$\text{(III)} + C_6H_5NH_2 \rightarrow \underset{\text{(IV)}}{ArCH{=}C(CN){-}CON{=}PR(NHC_6H_5)_2}$$

$$\text{(III)} + 2HCOOH \rightarrow \underset{\text{(V)}}{ArCH{=}C(CN){-}CONHP({=}O)R(OH)}$$

Ar, a = C_6H_5 ; b = *p*-$CH_3OC_6H_4$; c = *p*-ClC_6H_4 ; d = *m*-$NO_2C_6H_4$; e = *p*-$NO_2C_6H_4$; R = *p*-$CH_3C_6H_4$

Experimental

Melting points are uncorrected. I.R. spectra were recorded on a Beckman IR-5A unit as KBr pellets. *p*-Tolyldichlorophosphine[3] and arylidenecyanoacetamides[4] were prepared according to known procedures.

N-(Arylidenecyanoacetyl)-p-tolylphosphonimidic dichlorides(II) :

General Procedure :

A suspension of 0.01 mole of arylidenecyanoacetamides and 0.01 mole of *p*-tolyltetrachlorophosphorane in 50 ml carbon tetrachloride was refluxed until HCl evolution ceased, (ca., 1.5 hr), during which complete dissolution of the compounds

TABLE 1—N-(ARYLIDENECYANOACETYL)-*p*-TOLYLPHOSPHORIMIDIC DICHLORIDES(III) AND DIANILIDES(IV)

$$R{-}C_6H_4CH{=}C(CN){-}CON{=}P(C_6H_4CH_3\text{-}p)X_2$$

Compd.	R	Yield %	m.p. °C	X	Formula	Analysis Calcd.	Analysis Found	I.R.[a] νN=P
						%Cl	%Cl	
IIIa	H	80	71	Cl	$C_{17}H_{13}Cl_2N_2OP$	19.56	19.40	1294
b	*p*-CH_3O	78	144	Cl	$C_{18}H_{15}Cl_2N_2O_2P$	18.07	18.27	1286
c	*p*-Cl	85	142	Cl	$C_{17}H_{12}Cl_3N_2OP$	26.79	26.54	1295
d	*m*-NO_2	76	165	Cl	$C_{17}H_{12}Cl_2N_3O_3P$	17.40	17.21	1298
e	*p*-NO_2	73	187	Cl	$C_{17}H_{12}Cl_2N_3O_3P$	17.40	17.17	1300
						%N	%N	
IVa	H	92	195	C_6H_5NH	$C_{29}H_{25}N_4OP$	11.76	11.69	1311
b	*p*-CH_3O	86	184	C_6H_5NH	$C_{30}H_{27}N_4O_2P$	11.07	11.25	1305
c	*p*-Cl	88	200	C_6H_5NH	$C_{29}H_{24}ClN_4OP$	10.97	10.66	1312
d	*m*-NO_2	81	185	C_6H_5NH	$C_{29}H_{24}N_5O_3P$	13.44	13.21	1315
e	*p*-NO_2	83	206	C_6H_5NH	$C_{29}H_{24}N_5O_3P$	13.44	13.23	1320

TABLE 2—N-(ARYLIDENECYANOACETYL)-p-TOLYLPHOSPHORAMIDIC ACIDS(V)

$$R-C_6H_4CH=\overset{CN}{\overset{|}{C}}-CONH\overset{O}{\overset{\|}{P}}(C_6H_4CH_3\text{-}p)(OH)$$

Compd.	R	Yield%	m.p.°C	Formula	Analysis Calcd. %N	Analysis Found %N	I.R.[4] νP=O
Va	H	60	108	$C_{17}H_{15}N_2O_3P$	8.59	8.79	1247
b	p-CH_3O	69	205	$C_{18}H_{17}N_2O_4P$	7.86	7.66	1244
c	p-Cl	70	199	$C_{17}H_{14}ClN_2O_3P$	7.77	7.56	1250
d	m-NO_2	62	124	$C_{17}H_{14}N_3O_5P$	11.32	11.44	1250
e	p-NO_2	63	209	$C_{17}H_{14}N_3O_5P$	11.32	11.57	1258

occurred. The solution was cooled to room temperature and the precipitate formed was collected and washed with carbon tetrachloride and crystallised from benzene or carbon tetrachloride. The prepared compounds are recorded in Table 1.

N-(Arylidenecyanoacetyl)-p-tolylphosphonimidic dianilides(IV) :

A solution of 4 mmol aniline in 10 ml benzene was gradually added at room temperature to a suspension of the dichlorides(III), 1 mmol in 30 ml benzene. The mixture was stirred at room temperature for 4 hr and then refluxed for 2 hr. The solid was filtered, dried, washed well with water, dil. HCl, water and then crystallised from ethanol in colorless needles (Table 1).

N-(Arylidenecyanoacetyl)-p-tolylphosphonamidic acids(V) :

A solution of 0.01 mole of the dichlorides(III) in dry benzene was treated with 0.02 mole of anhydrous formic acid. The mixture was kept at room temperature for 4 hr and then refluxed for 2 hr. The precipitated solid was collected and crystallised from ethanol (Table 2).

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Vol. LVII, November 1980, pp. 1106-1107

Synthesis of 2-(3′-pyridyl)-Y-pyrano-Benzofurans and 3′-hydroxy-2′-(3″-pyridyl)-Y-pyrano-Benzofurans

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Manuscript received 12 January 1980, accepted 9 July 1980

A few 2′-(3″-pyridyl)-Y-pyrano-benzofurans (IVa-c) and 3′-hydroxy-2′-(3″-pyridyl)-Y-pyrano-benzofurans (Va-c) were synthesised from *o*-hydroxyacetyl benzofurans.

BENZOFURAN and furano chromones have been known to possess various pharmacological activities[1-4]. Khellin—a furanochromone is well known for its physiological activity[5-7]. The synthesis of pyrano benzofurans-khellin analogs-with 3-pyridyl substituent at 2 position in pyrone ring, was undertaken with the expectation that it will modify the activity of khellin itself.

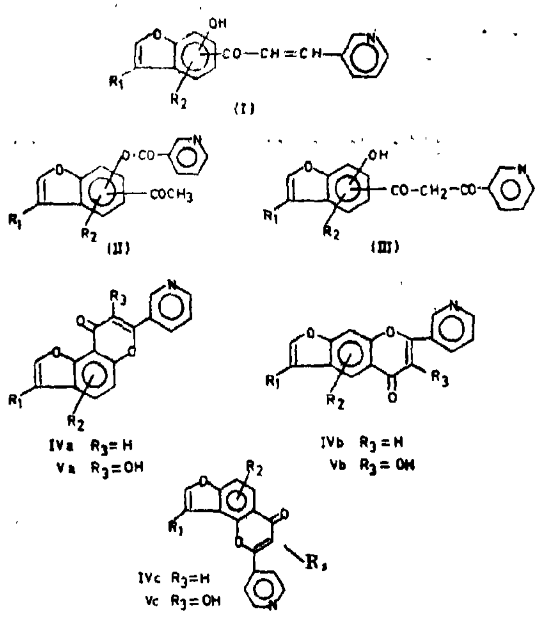
Pyridine-3-aldehyde on condensation with *o*-hydroxy-acetyl benzofurans in presence of a base yielded propan-1-ene-3-ones (I), which were converted into the corresponding substituted 2′-(3″-pyridyl)-Y-pyrano (7, 8-e) benzo furans (IVa), 2′-(3″-pyridyl)-Y-pyrano (7, 6-e) benzofurans (IVb) and 2′-(3″-pyridyl)-Y-pyrano (5, 6-e) benzofurans (IVc) by refluxing them with SeO_2 and amyl alcohol. These compounds (IV a-c) were also synthesised by an alternative route. The base catalysed esterification of *o*-hydroxy-acetyl benzofurans with nicotinoyl chloride yielded *o*-(3′-pyridiloxy)-acetyl-benzofurans (II). Baker-Venkatram transformation of these esters (II) yielded the corresponding propane 1 : 3 diones(III) which on cyclization gave the corresponding 2′-(3″-pyridyl)-Y-pyrano-benzofurans (IVa-c).

Propan-1-ene-3-ones (I) on subjecting to Algar-Flynn-Oyamada reaction conditions gave the corresponding 3′-hydroxy-2-pyridyl-Y-pyrano benzofurans (V a-c).

The melting points, crystallisation solvents, percentage yields, etc. of I, II, III, IV and V are given in Table 1.

Physiological activity :

The compounds were tested for antiviral activity, anthelmintic activity and gastric acid secretion pylorus ligation activity. None of the compounds showed these activities.



Experimental

o-Hydroxy-acetyl benzofurans were prepared by earlier reported methods[8-10].

General procedures for the preparation of :

Propan-1-ene-3-ones (I) : To a solution of pyridine-3-aldehyde (0.3 mole) and *o*-hydroxy-acetyl-benzofuran (0.2 mole) in ethanol (30 ml) was added slowly a solution of KOH (50%, 5 ml) maintaining the temperature below 25°. The reaction mixture was stirred for 3.4 hrs and it was then poured over crushed ice containing acetic acid. The solid obtained was filtered, washed with $NaHCO_3$ solution (5%) and crystallized from a proper solvent.

2′-(3″-Pyridyl)-Y-pyrano-benzofurans (IV a-c) : A mixture of propan-1-ene-3-one. (0.003 mole), SeO_2

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TABLE 1—PHYSICAL DATA OF PROPAN-1-ENE-3-ONES(I), o-(3'-PYRIDILOXY)-ACETYL-BENZOFURANS(II), PROPANE-1 3-DIONES(III), 2'-(3''-PYRIDYL)-Y-PYRANO-BENZOFURANS(IV) AND 3'-HYDROXY-2'-(3''-PYRIDYL)-BENZOFURANS(V)

Sl. No.	o-Hydroxy-acetyl benzofurans used	Corresponding Compounds									
		I		II		III		IV		V	
		m.p. °C	Yield %	m.p. °C	Yield %	m.p. °C	Yield %	m.p. °C	Yield %	m.p. °C	Yield %
(1)	6-Hydroxy-7-acetyl 3-methyl-benzofuran	171[a]	90	141[g]	80	153[g]	80	211[f]	80 (70)	198[c]	60
(2)	6-Hydroxy-7-acetyl 5-ethyl-3-methyl-benzofuran	138[e]	80	96[a]	60	118[g]	50	234[f]	70 (50)	188[d]	60
(3)	6-Hydroxy-5-acetyl 3-methyl-benzofuran	115[e]	90	143[c]	50	105[b]	30	232[f]	90 (30)	330[c]	40
(4)	6-Hydroxy-5-acetyl 4,7-dimethoxy-benzofuran	80[c]	95	79[b]	70	91[b]	60	182[f]	20 (20)	212[e]	70

* All compounds showed satisfactory C and H analysis.

a—Crystallised from 40% acetic acid ;
b—Crystallised from 50% acetic acid ;
c—Crystallised from 60% acetic acid ;
d—Crystallised from 70% acetic acid ;
e—Crystallised from 80% acetic acid ;
f—Crystallised from dioxane and
g—Crystallised from benzene.

(1 g) and amyl alcohol (14 ml) was refluxed for 10 hrs in an oil-bath at 150°. The solution was filtered hot and amyl alcohol was removed by steam distillation. The resulting solid was crystallised from a proper solvent.

3'-Hydroxy-2'-(3''-pyridyl)-Y-pyrano-benzofurans (V a-c) :

A solution of propan-1-ene-3-one (0.0014 mole) in methanol (15 ml) was added to an ice-cold solution of sodium hydroxide (16%, 2 ml) followed by dropwise addition of H_2O_2 (15%, 2 ml). The reaction mixtures was kept in an ice-chest overnight and filtered. The alkaline filtrate was acidified with acetic acid and precipitated solid was filtered, washed with water and crystallised from a proper solvent.

Esters (II) : To an ice-cold solution of o-hydroxy-acetyl-benzofuran (0.035 mole) in dry pyridine (10 ml), nicotinoyl chloride (0.04 mole) was added dropwise with stirring. The mixture was stirred for 7 hrs at room temperature and then poured over crushed ice containing acetic acid. The resulting solid was filtered, washed with NaOH (2%) and crystallised from a proper solvent.

Propane-1,3-diones (III) : A mixture of ester (0.025 mole), powdered KOH, (3.4 g) and dry pyridine (15 ml) was stirred vigorously for 6 hrs. It was then poured over ice-water and neutralised with acetic acid. The solid thus obtained was filtered, washed with water and crystallised from a proper solvent.

2'-(3''-Pyridyl)-Y-pyrano-benzofurans (IV a-c) : To an ice-cold solution of propane-1,3-dione (0.04 mole) in chloroform (40 ml), conc. H_2SO_4 (10 ml) was added slowly with stirring. The mixture was stirred further for 30 min at 20° and poured over ice-containing NaOH. The chloroform layer was separated and product was isolated by evaporation of the chloroform. The resulting solid was crystallised to form a proper solvent.

Acknowledgement

We are grateful to Dr. George Redl of SK & F Laboratories, Philadelphia (U.S.A.) for providing the physiological activities of the compounds.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1108-1111

Synthesis of Some N₁-Substituted-3,5-Dimethyl Pyrazoles and N₁-Substituted-3-Methyl-5-Pyrazolones and Rleated Compounds as Potential Fungicides

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Manuscript received 29 February 1980, revised 4 August 1980, accepted 7 August 1980

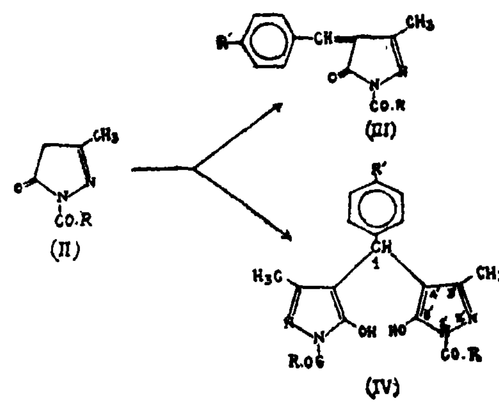
Six N_1-aroyl/aryloxyacetyl-3,5-dimethylpyrazoles, ten N_1-aroyl/aryloxyacetyl-3-methyl-5-pyrazolones, twenty N_1-aroyl/aryloxyacetyl-3-methyl-4-arylideno-2-pyrazoline-5-ones and five 1-aryl-1,1-*bis*-[N_1'-aroyl/aryloxyacetyl-3'-methyl-5'-hydroxy pyrazol-4'-yl]-methanes were prepared. Thirty two compounds have been screened against *A. flavus* and *A. niger* and found to possess moderate to fairly good antifungal activity.

SUBSTITUTED pyrazoles have been reported as anticancer[1], antifungal[1,2], insecticidal[3] and effective antibacterial[4] agents. Various 1-aryloxyalkyl pyrazoles have been evaluated as hypoglycemic, antiinflammatory and antiviral agents[5]. Many 1,3-disubstituted pyrazol-5-ones and derivatives are known to possess significant fungicidal[2,6] and antibacterial[7,8] activities. In view of this we have synthesised the title compounds which are expected to show enhance pesticidal activity due to presence of an aryloxyacetyl/carbonyl moiety.

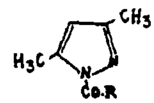
N_1-Aroyl/aryloxyacetyl-3,5-dimethyl pyrazoles(I) have been prepared by reaction of acetylacetone and aroyl/aryloxyacetyl hydrazines. N_1-Aroyl/aryloxyacetyl-3-methyl-5-pyrazolones(II) were prepared by refluxing a mixture of ethylacetoacetate and aroyl/aryloxyacetyl hydrazines. Pyrazolone(II) reacts with an aryl aldehyde in presence of fused sodium acetate and acetic acid to yield corresponding mono-arylidene derivative(III), while similar condensation in presence of piperidine afforded *bis*-pyrazolyl methane(IV). The compounds (IV) gave violet colouration with ferric chloride and show no >C=O absorption but a broad peak at ~3400 cm⁻¹ in IR spectra indicating the presence of enolic hydroxyl group.

The compounds were authenticated by elemental analyses, IR spectra and molecular weight determinations.

The compounds thus prepared are given in Tables 1-4 along their antifungal data. All the compounds gave consistent N, analysis.



SCHEME 1



(I)

Experimental

Aroyl/aryloxyacetyl hydrazines :

These were prepared by the method of Conti[9].

N_1-Aroyl/aryloxyacetyl-3,5-dimethyl pyrazoles (I)[10] *:*

A mixture of an ethanolic suspension (20 ml) of aroyl/aryloxyacetyl hydrazine (0.01 *M*) and acetylacetone (0.01 *M*) was refluxed gently for two hours.

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TABLE 1—N_1-AROYL/ARYLOXYACETYL-3,5-DIMETHYL PYRAZOLES(I)

No.	R	m.p. °C	Yield %	Fungicidal activity Concn. 10 ppm A. flavus	A. niger
1.[a]	4-Cl.C_6H_4	288	62.1	38.4	36.6
2.	2-HO.C_6H_4	306	33.8	28.3	25.4
3.	1-C_6H_5NH.C_6H_4	viscous liquid	53.5	—	—
4.	2-CH_3.C_6H_4-O-CH_2	171	20.4	—	—
5.[b]	4-CH_3.C_6H_4-O-CH_2	242	45.9	48.5	45.0
6.	4-$(CH_3)_3$C.C_6H_4-O-CH_2	330	45.4	75.7	74.4

IR spectral data ν_{max} in cm^{-1}

	–C(=O)–N<	–C=N–	=C–O–C–	p-disubstituted benzene	C–Cl
a	1600	1490	—	810	780
b	1700	1600	1240	825	—

TABLE 2—N_1-AROYL/ARYLOXYACETYL-3-METHYL-5-PYRAZOLONES(II)

No.	R	m.p. °C	Yield %	Fungicidal activity Concn. –10 ppm A. flavus	A. niger
7.	4-Cl.C_6H_4	95	89.8	31.6	27.5
8.	2-HO.C_6H_4	146	95.0	24.7	22.4
9.	2-C_6H_5NH.C_6H_4	31	78.3	27.3	24.8
10.[c]	C_6H_5-O-CH_2	62	93.9	33.4	29.6
11.	2-CH_3.C_6H_4-O-CH_2	94	94.7	36.7	31.2
12.	4-CH_3.C_6H_4-O-CH_2	85	96.4	37.4	33.0
13.	2-Cl.C_6H_4-O-CH_2	150	87.2	—	—
14.[d]	4-Cl.C_6H_4-O-CH_2	100	97.0	45.8	40.4
15.	4-$(CH_3)_3$C.C_6H_4-O-CH_2	101	84.0	69.5	65.2
16.	2-$(CH_3)_2$CH-5-CH_3.C_6H_3-O-CH_2	89.90	96.5	64.3	62.7

IR Spectral data ν_{max} in cm^{-1}

	Ring >C=O	–CON<	–C=N–	=C–O–C–	C–Cl
c	1690	1600	1500	1220	—
d	1725	1700	1600	1280	755

TABLE 3—N_1-AROYL/ARYLOXYACETYL-3-METHYL-4-ARYLIDENO-2-PYRAZOLINE-5-ONES(III)

No.	R	R′	m.p. °C	Yield %	Fungicidal activity Concn. –10 ppm A. flavus	A. niger
17.	2-HO.C_6H_4	H	170	65.3	36.8	34.0
18.[e]	2-HO.C_6H_4	Cl	186	65.3	42.0	38.5
19.	2-HO.C_6H_4	HO	266	71.4	37.3	34.8
20.	2-HO.C_6H_4	$(CH_3)_2$N	228	66.2	—	—
21.	C_6H_5-O-CH_2	H	146	56.2	48.0	39.8
22.	C_6H_5-O-CH_2	Cl	128	56.2	46.8	43.5
23.	C_6H_5-O-CH_2	HO	245	44.0	—	—
24.	C_6H_5-O-CH_2	$(CH_3)_2$N	110	65.3	44.2	42.2
25.	2-CH_3.C_6H_4-O-CH_2	H	122	56.3	—	—
26.	2-CH_3.C_6H_4-O-CH_2	Cl	108	67.0	48.2	44.8
27.	2-CH_3.C_6H_4-O-CH_2	HO	165	48.5	39.3	37.6
28.	2-CH_3.C_6H_4-O-CH_2	$(CH_3)_2$N	168	55.2	48.2	40.5
29.[f]	4-CH_3.C_6H_4-O-CH_2	H	136	54.5	—	—
30.	4-CH_3.C_6H_4-O-CH_2	Cl	116	67.4	50.6	48.8
31.	4-CH_3.C_6H_4-O-CH_2	HO	218[d]	48.0	42.4	38.6
32.	4-CH_3.C_6H_4-O-CH_2	$(CH_3)_2$N	115	62.0	—	—
33.	4-Cl.C_6H_4-O-CH_2	H	115	54.5	—	—
34.[g]	4-Cl.C_6H_4-O-CH_2	Cl	135	48.3	62.3	56.7
35.	4-Cl.C_6H_4-O-CH_2	HO	242[d]	45.6	47.1	43.6
36.	4-Cl.C_6H_4-O-CH_2	$(CH_3)_2$N	120	53.6	56.0	50.4

IR Spectral data ν_{max} in cm^{-1}

	–CH=C–	Ring >C=O	–CON<	–C=N–	=C–O–C–	C–Cl
e	3200	1675	1600	1500	—	735
f	3000	1690	1600	1500	1225	—
g	3050	1700	1600	1520	1230	750

TABLE 4—1-ARYL-1,1-*bis*-[N_1'-AROYL/ARYLOXYACETYL-3'-METHYL-5'-HYDROXYPYRAZOL-4'-YL]-METHANES(IV)

No.	R	R'	m.p. °C	Yield %	Molecular weight Found	Calcd.	Fungicidal activity Concn. 10 ppm *A. flavus*	*A. niger*
37.[h]	2-HO.C_6H_4	H	68	88.8	589	524	41.3	86.5
38.	4-Cl-C_6H_4	$(CH_3)_2N$	66	66.2	620.4	604	45.7	89.2
39.	4-CH_3-C_6H_4-O-CH_2	HO	75	67.7	608.7	596	46.8	41.3
40.[i]	2-Cl.C_6H_4-O-CH_2	$(CH_3)_2N$	158	77.1	678.2	664	68.6	57.6
41.	2-$(CH_3)_2$CH-5-CH_3.C_6H_3-O-CH_2	Cl	108	57.4	716.5	698	68.5	64.2
	MEMCGE						75.4	87.4
	BLITOX 50 WP (Commercial fungicides)						85.5	80.7

IR Spectral data ν_{max} *in* cm^{-1}

	–OH stretching	–CON<	–C=N–	=C–O–C–	*o*-disubstituted benzene
h	3360	1600	1570	—	730
i	3400	1650	1585	1250	735

To this acetic acid (5 ml) was added and the mixture refluxed further for one hour. A clear solution resulted. On evaporation a solid was obtained which was washed and recrystallised with aqueous ethanol.

N_1-Aroyl/aryloxyacetyl-3-methyl-5-pyrazolones (II)[11] *:*

A mixture of an ethanolic suspension (20 ml) of aroyl/aryloxyacetyl hydrazine (0.01 *M*) and ethylacetoacetate (0.01 *M*) was refluxed gently for three hours. A clear solution resulted. On evaporation a solid was obtained which was washed and recrystallised with aqueous ethanol.

N_1-Aroyl/aryloxyacetyl-3-methyl-4-arylideno-2-pyrazoline-5-ones(III) :

An aroyl/aryloxyacetyl-3-methyl-5-pyrazolone (0.01 *M*) was dissolved in a minimum of glacial acetic acid. To this fused sodium acetate (2.0 g) and an aryl aldehyde (0.01 *M*) were added and the mixture refluxed for six hours. It was cooled and poured into cold water. The solid separating out was filtered, washed and recrystallised from aqueous ethanol.

The monoarylidene compounds (III) decolourise bromine water and their formation is further supported by the molecular weight, IR spectra and the elemental analysis results.

1-Aryl-1,1-bis-[N_1'-aroyl/aryloxyacetyl-3'-methyl-5'-hydroxy pyrazol-4'-yl]-methanes (IV) :

A methanolic solution of aroyl/aryloxyacetyl-3-methyl-5-pyrazolone (0.01 *M*) and aryl aldehyde (0.005 *M*) was treated with few drops of piperidine and kept at room temperature for several hours till a crystalline solid separated out. It was filtered off, washed and recrystallised from ethanol.

The *bis*-pyrazolyl methanes(IV) gave violet colour with ferric chloride solution. Their formation is further supported by the absence of >C=O absorption but presence of a broad peak at ~3400 cm^{-1}, characteristic of enolic hydroxyl group in the IR spectra. The molecular weights of compounds (IV) were also in agreement with *bis* structure.

Fungicidal Screening :

The compounds were screened for their antifungal activity against *A. flavus* and *A. niger* by agar plate technique[12,13] at three different concentrations viz. 1000 ppm, 100 ppm and 10 ppm. Two commercial fungicides MEMCGE and BLITOX 50 WP have also been tested under similar conditions to compare the result. The number of replications in each case was three. The percentage inhibition of growth of fungus colony is given by expression :

$$\text{Percentage inhibition} = \frac{C - T \times 100}{C}$$

where C = diameter of fungus colony (in mm) in control after 96 hours,

T = diameter of fungus colony (in mm) in presence of test chemical after 96 hours.

Results and Discussion

Most of the compounds screened possess moderate to fairly good level of fungicidal activity against both the fungi. The pyrazole(I) No. 6[R = 4–$(CH_3)_3$C.C_6H_4–O–CH_2–], pyrazolones(II Nos. 15 and 16[R = 4–$(CH_3)_3$C.C_6H_4–O–CH_2–

2-$(CH_3)_2CH-5-CH_3.C_6H_3-O-CH_2-$], monoarylideno pyrazolone(III) No. 34[$R=4-Cl.C_6H_4-O-CH_2-$, $R'=Cl$] and *bis*-pyrazolyl methanes(IV) Nos. 40 and 41 [$R=2-Cl.C_6H_4-O-CH_2-$, $R'=(CH_3)_2N$; $R=2-(CH_3)_2CH-5-CH_3.C_6H_3-O-CH_2-$, $R'=Cl$] inhibit >60% mycelial growth of both the fungal species even at 10 ppm concentration and display antifungal activity of the order of MEMCGE and BLITOX 50 WP at 1000 and 100 ppm concentrations. In general, pyrazoles(I) are slightly better fungicide than the corresponding pyrazolones(II). Further, *bis*-pyrazolyl methanes(IV) are more active than the corresponding monoarylidenopyrazolones(III), which are relatively more potent than the corresponding pyrazolones(II). Introduction of an aryloxyacetyl group at N_1 position invariably increases the antifungal activity of the compound.

Acknowledgement

The author sincerely thanks Prof. R.P. Rastogi, Head, Chemistry Department, Gorakhpur University and Dr. Y. B. Singh, Principal, St. Andrew's College, Gorakhpur for providing the necessary facilities.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1112-1114

Heterocyclic Systems with Bridgehead Nitrogen Atom : Reactions of 4-amino-5-mercapto-3-substituted-*s*-triazoles with Haloketones, Carboxylic acids and α-halo acids

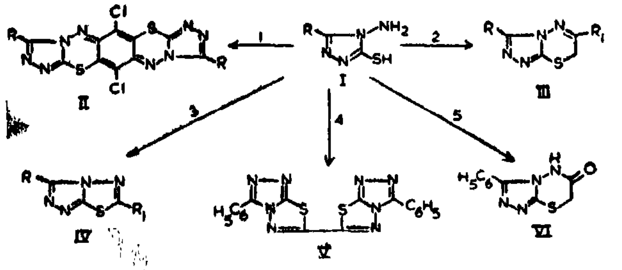
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Manuscript received 24 March 1980, accepted 7 August 1980

The reaction of 4-amino-5-mercapto-3-substituted-*s*-triazoles(I) with chloranil and α-haloketones furnished 3, 10-disubstituted-6, 13-dichloro, *bis*(*s*-triazolo[3,4 : 2',3'] [1,3,4] thiadiazino[5',6'-*b* : 5',6'-*e*]) cyclohexa-1,4-diene(II) and 7*H*-3,6-disubstituted-*s*-triazolo[3,4-*b*][1,3,4] thiadiazoles(III) respectively. Similarly reaction of I with aromatic carboxylic acids and oxalic acid in presence of phosphorous oxychloride gave *s*-triazolo [3,4-*b*][1,3,4] thiadiazoles(IV) and 6,6'-*bis*(3,6-diphenyl-*s*-triazolo [3,4-*b*][1,3,4] thiadiazoles(V) respectively, whereas with α-chloroacetic acid afforded 7*H*-3-phenyl-*s*-triazolo [3,4-*b*][1,3,4] thiadiazin 6(5*H*)-one(VI). Some of the compounds were screened for their antitumor activity.

IN continuation to our work on the syntheses of Bridgehead nitrogen heterocycles[1-4], the present communication deals with the syntheses of some new 3,10-disubstituted-6, 13-dichloro-*bis*-(*s*-triazolo [3, 4 : 2', 3'][1,3,4] thiadiazino[5',6'-*b* : 5',6'-*e*] cyclo haxa-1, 4-dienes(II), 3, 6-disubstituted-*s*-triazolo [3,4-*b*][1,3,4] thiadiazines(III), *s*-triazolo[3,4-*b*] [1,3,4] thiadiazoles(IV), 6,6'-*bis* (3,6-diphenyl-*s*-triazolo[3,4-*b*][1,3,4] thiadiazole(V) and 7*H*-3-phenyl-*s*-triazolo[3,4-*b*][1,3,4]-thiadiazine 6(5*H*)-one(VI) respectively. Thus I when condensed with chloranil in presence of fused sodium acetate and anhydrous ethanol yielded II, whereas with α-haloketones furnished III. *s*-Triazolo [3,4-*b*][1,3,4] thiadiazoles have been synthesized by Golgolab *et al*[5]. I when reacted with aromatic carboxylic acids and oxalic acid in presence of phosphorous oxychloride gave IV and V respectively. Reaction of I ($R=C_6H_5$) with mono-chloro-acetic acid in presence of anhydrous sodium acetate and absolute alcohol furnished(VI). The spectral character of compounds II, III, IV, V and VI are also consistent with the structures proposed for them (vide experimental).



1. Chloranil, EtOH, NaOAc ; 2. R_1COOH_2X, EtOH, NaOAc , 3. R_1COOH, $POCl_3$; 4. Oxalic acid, $POCl_3$ & 5. $ClCH_2COOH$, EtOH, NaOAc.

*For Correspondence.

Compounds II ($R=CH_3$, C_2H_5, *o*-HO-C_6H_4) and III ($R=$*o*-HO-C_6H_4, $R_1=C_6H_5-C_6H_4$; $R=CH_3$, $R_1=C_6H_5-C_6H_4$; $R=C_2H_5$, $R_1=C_6H_5-C_6H_4$) have been screened for their biological evaluation as possible anticancer agents. However none of the compounds showed any significant activity when tested against P 388 *lymphocytic leukemia in vivo*.

Experimental

Melting points are uncorrected. IR spectra were taken on Beckman I.R.-20 spectrophotometer in Nujol mull.

3-o-Hydroxyphenyl-4-amino-5-mercapto-s-triazole (I, $R=o$-HO$-C_6H_4$) :

This was prepared by heating under reflux *o*-hydroxy benzoyl-dithiocarbazinate (5.32 g, 0.02 mole) and hydrazine-hydrate 80% (10 ml) for about two hours. The colour of the reaction mixture changed to green, hydrogen sulphide was evolved resulting in a homogeneous solution. The reaction mixture was cooled, diluted with water and neutralized with conc. HCl. The white precipitate thus obtained was filtered, washed with water and crystallized from aqueous ethanol in colourless needles. m.p. 208-09°. Yield 60% (2.5 g). I.R. ν_{max} (cm^{-1}) 3290, 3080, 1630, 1580, 1495, 1160, 1020, 760, 690 (Found : S, 14.96. $C_8H_8N_4SO$ requires S, 15.38%).

3-Phenyl-4-amino-5-mercapto-s-triazole(I, $R=C_6H_5$) :

It was prepared by the method of Reid and Heindel[6].

3-Alkyl substituted-4-amino-5-mercapto-s-triazoles :

These were synthesized by refluxing a mixture of thiocarbohydrazide and the corresponding aliphatic acids as described in the literature[7,8].

3-10-Diethyl-6,13-dichloro-bis(s-triazolo [3,4 : 2',3'] [1,3,4] thiadiazino [5',6'-b : 5',6'-e] Cyclohexa-1, 4-diene (II, R = C_2H_5) :

I (R = C_2H_5, 2.88 g, 0.02 mole), chloranil (2.46 g, 0.01 mole) and anhydrous sodium acetate (1.64 g) in absolute ethanol (40 ml) were refluxed on a steam bath for about 4 hours. The reaction mixture acquired reddish colouration and a red coloured solid separated. The solid was filtered, washed thoroughly with water and a small amount was crystallized from DMF. m.p.>300°. Yield (58%). ν_{max}(cm^{-1}) 1650, 1535, 1150, 955, 835, 720 (Found : C, 39.88 ; H, 2.52 ; S, 14.86. $C_{14}H_{10}N_8S_2Cl_2$ requires C, 39.53 ; H, 2.35 ; S, 15.06%).

The other similar compounds prepared are below in Table 1.

TABLE 1—3,10-DISUBSTITUTED-6,13-DICHLORO-*bis*(s-TRIAZOLO[3,4 : 2',3'][1,3,4]THIADIAZINO[5',6'-*b* : 5',6'-*e*] CYCLOHEXA-1,4-DIENE(II)

R	m.p.°C	Yield
H	>300	50
C_3H_7	232-35	64
C_6H_5	>290	80
o-HO-C_6H_4	>300	75

7H-3(o-Hydroxyphenyl)-6-biphenyl-s-triazolo[3,4-b] [1,3,4]thiadiazine(III, R = o-HO − C_6H_4, R_1 = C_6H_5 − C_6H_4) :

I (R = HO − C_6H_4, 1.04 g, 0.005 mole), *p*-phenyl phenacyl bromide (1.38 g, 0.005 mole) and fused sodium acetate (0.5 g) in anhydrous ethanol (30 ml) was refluxed for about seven hours. The solid obtained on cooling was filtered, washed thoroughly with water and crystallized from acetic acid. m.p. 230°. Yield 1.6 g (80%). ν_{max}(cm^{-1}), 3500-3400, 1630, 1590, 1490, 1265, 830, 745, 700 (Found : S, 7.97 ; N, 14.14. $C_{22}H_{16}N_4SO$ requires S, 8.33 ; N, 14.58%).

The properties and analyses of other *s*-triazolothiadiazines(III) are described in Table 2.

3-Phenyl-6-p-nitrophenyl-s-triazolo [3,4-b] [1,3,4] thiadiazole (IV, R = C_6H_5, R_1 = p-O_2N − C_6H_4) :

A mixture of I, (R = C_6H_5, 0.96 g, 0.005 mole), *p*-nitro benzoic acid (1.67 g, 0.01 mole) and phosphorous oxychloride (10 ml) was refluxed for about one hour. The reaction mixture poured over crushed ice. The solid thus separated was filtered and treated with dilute sodium hydroxide solution to remove unreacted materials. Again filtered, washed with water and finally crystallized from acetic acid. m.p. 261°. Yield 1.40 g (86%). ν_{max} (cm^{-1}), 1610, 1525, 1350, 970, 850, 770, 685 (Found : S, 9.53, $C_{15}H_9N_5SO_2$ requires S, 9.91%).

TABLE 2—7H-3,6-DIARYL-s-TRIAZOLO[3,4-*b*][1,3,4]-THIADIAZINES (III, R *o*-HO-C_6H_4)

R_1	m.p. °C	Yield %
C_6H_5	212	71
p-Br-C_6H_4	232	64
m-O_2N-C_6H_4	265-70*	56
3,4(HO)$_2$$C_6H_3$	252-55*	67
p-Cl-C_6H_4	242	67

* Charring takes place.

The other *s*-triazolothiadiazoles prepared in this connection are given in Table 3.

TABLE 3—3,6-DISUBSTITUTED-s-TRIAZOLO [3,4-*b*][1,3,4]-THIADIAZINES(IV)

R	R_1	m.p. °C	Yield %
C_6H_5	m-$O_2NC_6H_4$	219	68
C_6H_5	3,5(O_2N)$_2$$C_6H_3$	>290	88
C_6H_5	o-Cl-C_6H_4	183	71
C_6H_5	p-Cl-C_6H_4	194	76
C_6H_5	C_6H_5-CH=CH	182-83	85
CH_3	p-O_2N-C_6H_4	262	69
CH_3	3,5(O_2N)$_2$$C_6H_3$	255	65
CH_3	p-Cl-C_6H_4	195	73

Bis-(3-phenyl-s-triazolo[3,4-b][1,3,4]-thiadiazole) (V) :

This was synthesized by reacting a mixture of I (R = C_6H_5, 3.84 g, 0.02 mole), oxalic acid (1.26 g, 0.01 mole) and phosphorous oxychloride (15 ml) following the above procedure. m.p.>300° (acetic acid). Yield 45%. ν_{max} (cm^{-1}), 1600, 1525, 960, 900, 760, 680 (Found : S, 15.71 ; N, 27.38. $C_{18}H_{10}N_8S_2$ requires S, 15.92 ; N, 27.86%).

7H-3-Phenyl-s-triazolo [3,4-b][1,3,4] thiadiazino-6 (5H)-one(VI) :

I(R = C_6H_5, 1.92 g, 0.01 mole), chloroacetic acid (1.0 g, 0.01 mole) and fused sodium acetate (0.82 g) taken in anhydrous ethanol (30 ml) were refluxed on a steam bath for 6 hours. The reaction mixture poured over water. The white solid filtered and crystallized from ethanol in colourless crystals, m.p. 185-86°. Yield 1.2 g (51.7 %). ν_{max} cm^{-1} 3340, 3270, 1720, 1610, 1520, 1350, 1200, 970, 890, 775, 690 (Found : S, 13.42 ; N, 23.86. $C_{10}H_8N_4SO$ requires S, 13.79 ; N, 24.14%).

Acknowledgement

The authors wish to express their sincere thanks to Prof. H. K. Pujari, Department of Chemistry, Kurukshetra University and Dr. M. R. Ghelra, Principal, Govt. Post-graduate College, Churu for encouragement, to the Director, Central Drug Research Institute, Lucknow for C,H analysis, to Dr. Robert, B. Ing. National Cancer Institute, Bethesda, Maryland, U.S.A., for antitumor screening and to the University Grants Commission, New Delhi for financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1115-1117

Syntheses of Triarylbutanes and Substituted Diaryl Alkanones†

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Manuscript received 31 May 1979, accepted 7 August 1980

Syntheses of 1,1,4-triarylbutanes, 3-alkyl-3,4-diaryl-butan-2-ones, 3,4-dialkyl-3,4-diaryl-butan-2-ones, 4-alkyl-4,5-diaryl-pentan-3-ones and 4,7-diphenyl-heptan-3-ones have been synthesised as possible antiprogestational agents. A plausible mechanism for the dialkylation in Grignard reaction of α-aryl-cinnamonitriles has been proposed.

IN a programme of research aimed towards obtaining non-steroidal antiprogestational agents, it was considered desirable to synthesize 1,1,4-triarylbutanes **(1-4)**, 3-alkyl-3,4-diaryl-butan-2-ones **(12-13 & 18-21)**, *erythro*-3,4-dialkyl-3,4-diaryl-butan-2-ones **(14-17)**, 4-alkyl-4,5-diaryl-pentan-3-ones **(5-10 & 22-24)** and 4,7-diphenyl-heptan-3-one **(11)** (Fig. 1, Table 1). These are described in this communication.

Reaction of benzophenone with sodium acetylide followed by the treatment with sulphuric acid yielded diphenyl acrolein which on further reaction with the sodium salt of phenylacetic acid in presence of acetic anhydride, cupric acetate and lead oxide yielded 1,1-diphenyl-4-aryl-1,3-butadienes[2]. Catalytic hydrogenation of these dienes furnished the desired 1,1-diphenyl-4-aryl butanes **(1-4)**. The desired butan-2-ones **(12-21)**, pentane-3-ones **(5-10 & 22-24)** and heptan-3-one **(11)** were obtained from substituted benzyl cyanides. The reaction of the latter with substituted benzaldehydes yielded α-aryl cinnamonitriles and with cinnamaldehyde yielded α-cinnamylidene-α-tolunitrile. The catalytic hydrogenation of these nitriles furnished α-aryl dihydro-cinnamonitriles and 2,5-diphenyl valeronitrile respectively. Reaction of α-aryl cinnamonitriles with excess of alkyl magnesium halides in dry ether yielded a mixture of diastereomeric α,β-dialkyl-α,β-diaryl propionitrile[1], the *erythro*-isomer of which on further reaction with methylmagnesium iodide in dry toluene yielded *erythro*-3,4-dialkyl-3,4-diaryl-butan-2-ones **(14-17)**. Grignard reaction of α-aryl dihydrocinnamonitriles in dry toluene yielded the desired 3,4-diaryl-butan-2-ones **(12-13** and **18-20)** and 4,5-diaryl-pentan-3-ones **(5-10 & 22)** as major products. Alkylation of α-aryldihydro cinnamonitriles followed by the Grignard reaction with ethylmagnesium bromide in dry toluene furnished the required 4-alkyl-4,5-diaryl-pentane-3-ones **(23-24)**. A rational explanation to explain the dialkylation in the Grignard reaction of α-aryl cinnamonitriles relates to the mode of addition of the Grignard reagent. Of the two probabilities of addition of alkylmagnesium halide to α-aryl cinnamonitriles, the 1,4-addition would alone furnish the β-alkylated derivative while the α,β-dialkylated product may appear from 3,4-addition of the Grignard reagent in two steps. The first step would lead to β-alkylation and the MgX component would then occupy the carbon-atom adjacent to the nitrile group. Mechanistically, such a situation would be favoured if the anion gets stabilised on the carbon α to the nitrile group. Since Collins have already shown that the negative charge rests on the adjacent carbon of the nitrile group[4], the proposed 3,4-addition of the Grignard reagent may be explained. The proposed halomagnesium complex obtained as a result of 3,4-addition of the Grignard reagent could then undergo further coupling reaction with the excess of alkylmagnesium halide present in the reaction mixture possibly by a non-ionic mechanism to yield the α,β-dialkylated derivative. Such a C – C coupling in the Grignard reaction has been reported earlier[5]. The evidence to the formation of a β-alkyl derivative at the beginning of the reaction was obtained by carrying out the Grignard reaction with exactly one mole of alkyl magnesium halide which gave predominantly a β-alkylated derivative (40%) and a minor amount of α,β-dialkylated derivative (0.6%). The formation of the proposed halomagnesium complex was evident from the reaction of alkylmagnesium halide with α-aryldihydrocinnamonitriles which furnished the α-alkylated derivative[3].

Experimental

Catalytic hydrogenation of 1,1-diphenyl-4-aryl butadiene :

The triaryl butadiene (0.002 mole) was hydrogenated in ethanol (15 ml) over 10% Pd – C (60 mg) at 40 lbs/sq. inch for 8 hrs. Usual work-up of the reaction mixture yielded the required compound **(1-4)** yield 75%.

† CDRI Communication No. 2529.

TABLE 1—PHYSICAL AND ANALYTICAL DATA OF VARIOUS KETONES

Comp. No.	R	m.p. (°C)	Molecular formula	Elemental Analysis % Required	Found
1	2	3	4	5	6
1.	*o*-tolyl	Oil	$C_{23}H_{24}$	C 91.95 H 8.05	91.75 8.25
2.	*p*-chlorophenyl	Oil	$C_{22}H_{21}Cl$	C 82.35 H 6.59	82.10 6.80
3.	*p*-methoxyphenyl	65-7	$C_{23}H_{24}O$	C 87.30 H 7.64	87.00 7.90
4.	*p*-hydroxyphenyl	86-7	$C_{22}H_{22}O$	C 87.38 H 7.33	87.68 7.72
		R_1 = phenyl, R_2 = Et			
5.	Phenyl	Oil	$C_{17}H_{18}O$	C 85.67 H 7.61	85.82 7.40
6.	2,4-dichlorophenyl	Oil	$C_{17}H_{16}Cl_2O$	C 66.46 H 5.25	66.75 5.40
7.	*p*-tolyl	Oil	$C_{18}H_{20}O$	C 85.67 H 7.99	85.20 8.18
8.	2,4-dimethoxyphenyl	Oil	$C_{19}H_{22}O_3$	C 76.48 H 7.43	76.72 7.25
9.	*p*-methoxyphenyl	Oil	$C_{18}H_{20}O_2$	C 80.56 H 7.51	80.70 7.75
10.	3,4-dichlorophenyl	Oil	$C_{17}H_{16}Cl_2O$	C 66.46 H 5.25	66.82 5.46
11.	Phenethyl	Oil	$C_{19}H_{22}O$	C 85.67 H 8.32	85.60 8.20
		R_1 = Phenyl, R_2 = Me			
12.	*p*-tolyl	Oil	$C_{17}H_{18}O$	C 85.67 H 7.61	85.75 7.71
13.	2,4-dimethoxyphenyl	Oil	$C_{18}H_{20}O_3$	C 76.03 H 7.09	76.40 7.28
		R_1 = Phenyl, R_2 = R_3 = R_4 = Me			
14.	*p*-methoxyphenyl	Oil	$C_{19}H_{22}O_2$	C 80.82 H 7.85	80.55 8.10
15.	2,4-dichlorophenyl	106-7	$C_{18}H_{18}Cl_2O$	C 67.29 H 5.64	67.70 5.85
16.	3,4-dichlorophenyl	Oil	$C_{18}H_{18}Cl_2O$	C 67.29 H 5.64	67.48 5.78
17.	Phenyl	Oil	$C_{18}H_{20}O$	C 85.67 H 7.99	85.80 8.10
		R_1 = *p*-chlorophenyl, R_4 = Me			
18.	*p*-benzyloxyphenyl	114-15	$C_{23}H_{21}ClO_2$	C 75.71 H 5.80	75.80 5.90
19.	*p*-(N,N-diethylamino)-ethoxyphenyl	Oil	$C_{22}H_{28}NClO_2$	C 70.66 H 7.54 N 3.74	70.50 7.70 3.80
20.	*m*-nitro-*p*-tolyl	Oil	$C_{17}H_{16}NClO_3$	C 64.25 H 5.06 N 3.74	64.46 5.20 3.90
		R_1 = Phenyl, R_2 = R_3 = Me			
21.	2,4-dimethoxyphenyl	Oil	$C_{19}H_{22}O_3$	C 76.48 H 7.43	76.80 7.62
		R_1 = *p*-chlorophenyl, R_2 = Et			
22.	Phenyl	Oil	$C_{17}H_{17}ClO$	C 74.85 H 6.28	75.10 6.52
		R_1 = Phenyl, R_2 = Et, R_3 = Me			
23.	Phenyl	Oil	$C_{18}H_{20}O$	C 85.67 H 7.99	86.00 8.20
		R_1 = Phenyl, R_2 = Et, R_3 = *n*-amyl			
24.	Phenyl	Oil	$C_{22}H_{28}O$	C 85.66 H 9.15	85.70 9.36
		R_1 = R_2 = R_3 = R_4 = Nil			
25.	*n*-amyl	Oil	$C_{20}H_{23}N$	C 86.59 H 8.36 N 5.05	86.80 8.66 5.25

Alkylation of α-phenyldihydrocinnamonitrile (**25**) :

To a suspension of sodamide (0.022 mol) in dry ether (40 ml) was added under stirring a solution of the α-phenyldihydrocinnamonitrile (0.020 mol) in dry ether (50 ml) and the reaction mixture was refluxed for 2 hrs. It was then cooled in an ice bath and to this was added carefully the amyl bromide (0.04 mole). After the addition was complete the reaction mixture was refluxed for 15 hrs, cooled and was decomposed with dilute HCl. The organic layer was washed with water, dried over anhydrous sodium sulphate and the solvent distilled off. The residue was purified by column chromatography over silica using hexane as the eluant, yield 70%.

Grignard reaction of α-aryldihydrocinnamonitrile :

To a solution of alkylmagnesium halide (0.075 mol) prepared by the reaction of magnesium (0.075 gm atom) and alkyl halide (0.075 mol) in dry ether (50 ml) was added a solution of α-aryldihydrocinnamonitrile (0.025 mol) in dry toluene (120 ml). The temperature of the reaction mixture was slowly raised to 100° to drive away the ether present in the mixture. The clear solution was then refluxed for 36 hrs, cooled and decomposed with sulphuric acid (4*N*). The organic layer was washed with water, drid over anhydrous sodium sulphate and the removal of the solvent under vacuo followed by repeated chromatography of the residue over silica gel using hexane as the eluant yielded the desired product **12-13**, **18-20** & **5-11**, yield 40-65%. In one case the yield of the α-alkylated ketone (**21**) was more than the yield observed in other cases.

Grignard reaction of α-alkyl-α,β-diaryl propionitrile and erythro-α,β-dialkyl-α,β-diaryl propionitrile :

Following the procedure described above α-alkyl-α,β-diaryl propionitrile yielded the required ketones (**23-24**), yield 60%, while *erythro*-α,β-dialkyl-α,β-diaryl propionitrile yielded the corresponding erythro ketones (**14-17**), yield 60-70%.

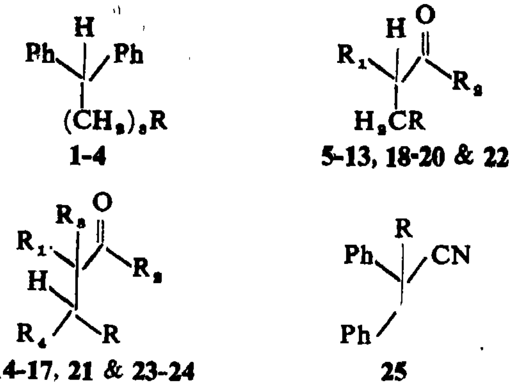


Fig. 1.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1118-1120

Antimicrobial Agents—Part IV+ : Synthesis and Antimicrobial Activity of Some New Arylsulfonylhydrazones Derived from 5-Substituted-2-Furaldehydes and 3-(5-Nitro-2-Furyl) Acrolein‡

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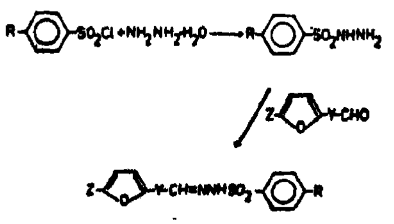
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Manuscript received 10 October 1979, revised 7 April 1980, accepted 7 August 1980

Several new arylsulfonylhydrazones derived from variously 5-substituted-2-furaldehydes and 3-(5-nitro-2-furyl) acrolein have been synthesized and screened *in vitro* for their antibacterial and antifungal activities.

ARYLSULFONYLHYDRAZONES of 2-furaldehyde and 5-nitro-2-furaldehyde have been reported to possess antibacterial activity[1] and are also useful as anticoccidial agents[2] in poultry. A recent communication by Juneau *et al*[3] on some arylsulfonylhydrazones derived from various heterocycles has prompted us to report our work on the synthesis and antimicrobial screening of a number of new related hydrazones of 5-substituted-2-furaldehydes and 3-(5-nitro-2-furyl) acrolein, prepared as a part of our continued search for biologically active furan derivatives[4-6], corresponding to structure I.

The various arylsulfonyl hydrazides required as starting materials were prepared by reacting the respective sulfonyl chlorides with 80% $NH_2NH_2.H_2O$ in THF following the standard procedures[7]. However *p*-aminobenzenesulfonyl hydrazide was obtained from its sulfonyl fluoride[8] according to



I

the method of Jensen[9]. Although 5-butylthio-2-furaldehyde was reported in literature[10], its physical characteristics were not described. It has now been prepared by us by the condensation of 5-bromo-2-furaldehyde with butanethiol in boiling toluene in the presence of sodium methoxide and was characterized through its semicarbazone. 5-(*p*-Nitrophenyl)-2-furaldehyde[11] and 3-(5-nitro-2-furyl) acrolein[12] were made according to known methods, while 5-(*p*-nitrophenoxy)- and 5-(*p*-chlorophenoxy)-2-furaldehydes were prepared as described earlier[13].

The desired arylsulfonylhydrazones(I) were synthesized in excellent yields (Table 1) by reacting the respective sulfonyl hydrazides with appropriate aldehyde and were isolated as bright yellow crystalline solids. These compounds were characterised by their mode of synthesis and elemental analyses. Their structures were further confirmed by IR spectra, which showed the characteristic absorption bands around 3,180-3,200 (NH) and 1360-1380 and 1160-1180 cm^{-1} ($-SO_2-$).

All the compounds reported in Table 1 were screened *in vitro* for their antibacterial and antifungal activities.

Experimental

Melting points were determined in closed glass capillary tubes using sulfuric acid bath and are uncorrected. IR spectra were recorded in nujol on a Perkin-Elmer 237 grating spectrophotometer. Elemental analyses were performed using Hösli Microcombustion apparatus MK 101.

5-Butylthio-2-Furaldehyde :

Sodium methoxide (5.4 g, 0.1 mol) in absolute methanol (40 ml) and butanethiol (9.0 g, 0.1 mol) were added simultaneously dropwise into dry toluene (80 ml) and the mixture was heated at 60-80° for 15 minutes. To this was added dropwise a solution of 5-bromo-2-furaldehyde (17.5 g,

+ Part III, *J. Indian Chem. Soc.*, 1979, 56, 74.

‡ Communication No. 31 from IDPL Research Centre, Hyderabad.

TABLE 1—ARYLSULFONYLHYDRAZONES (I*)

Comp. No.	Z	Y	R	m.p. °C	Yield %	Solvent of Crystallization
1.	SC_4H_3	—	CH_3	82-84	82	MeOH
2.	SC_4H_3	—	Cl	124-26	81	MeOH
3.	SC_4H_3	—	NH_2	94-96	78	EtOAc-Pet. ether
4.	SC_4H_3	—	$NHCOCH_3$	190-92	90	MeOH
5.	p-$NO_2C_6H_4$	—	CH_3	204-06d	82	AcOH
6.	p-$NO_2C_6H_4$	—	Cl	206-07d	79	AcOH
7.	p-$NO_2C_6H_4$	—	NH_2	210d	76	EtOAc-Pet. ether
8.	p-$NO_2C_6H_4$	—	$NHCOCH_3$	206-28d	82	AcOH
9.	p-$NO_2C_6H_4-O-$	—	CH_3	172-73	87	AcOH
10.	p-$NO_2C_6H_4-O-$	—	Cl	182-83	82	AcOH
11.	p-$NO_2C_6H_4-O-$	—	NH_2	170-71	70	EtOAc-Pet. ether
12.	p-$NO_2C_6H_4-O-$	—	$NHCOCH_3$	192d	92	AcOH
13.	p-ClC_6H_4-O-	—	CH_3	123-25	80	EtOAc-Pet. ether
14.	p-ClC_6H_4-O-	—	Cl	144-46	80	EtOAc-Pet. ether
15.	p-ClC_6H_4-O-	—	NH_2	190-92	66	EtOAc
16.	p-ClC_6H_4-O-	—	$NHCOCH_3$	184-86	92	MeOH
17.	NO_2	CH=CH	CH_3	132-34	90	MeOH
18.	NO_2	CH=CH	Cl	158-60	79	MeOH
19.	NO_2	CH=CH	NH_2	142-44	72	MeOH
20.	NO_2	CH=CH	$NHCOCH_3$	206-08d	86	MeOH

* Satisfactory analysis for C, H and N were obtained.
d Decomposition.

0.1 mol) in dry toluene (40 ml) during 0.5 hr with stirring. The reaction mixture was heated under reflux at 120-130° for 4 hr in an oil bath. The contents were then cooled to 50°, filtered to remove NaBr and the solvent was removed under reduced pressure. The residue was distilled under vacuum to yield 11 g (59%) of the title compound as colourless liquid, b.p. 126-128° (10 mm) ; Semicarbazone ; m.p. 128-130° (MeOH) (Found : C, 49.44 ; H, 5.97 ; N, 17.66. $C_{10}H_{15}N_3O_2S$ requires C, 49.79 ; H, 6.22 ; N, 17.43%).

Arylsulfonylhydrazones (I, Table 1) :

General procedure :

A mixture of arylsulfonylhydrazide (0.01 mol) and appropriate aldehyde (0.01 mol) in methanol (50 ml) was refluxed for 3 hr. The reaction mixture was concentrated under reduced pressure and cooled in ice. The resulting solids were filtered, washed with methanol and recrystallized from suitable solvent (Table 1) to give the pure compounds as bright yellow crystalline solids.

Biological screening results :

All the compounds reported in Table 1 were tested *in vitro* for their antibacterial activity by serial dilution tube method and antifungal activity by agar dilution assay method as described earlier[4]. The highest dilution of the test compound which inhibited the visual growth of the organism was taken as minimum inhibitory concentration (MIC, μg/ml). The bacteria employed were *S. aureus*, *S. typhi*, *E. coli*, *A. tumefaciens*, *B. subtilis* and *M. tuberculosis* H_{37}RV and the fungi used were *C. albicans*, *Cr. neoformans*, *T. mentagrophytes*, *M. canis* and *A. niger*.

Out of all the compounds studied, the arylsulfonylhydrazones derived from 3-(5-nitro-2-furyl) acrolein alone showed moderate antimicrobial activity, while the remaining were completely inactive against all the organisms at the maximum test concentrations (100 μg/ml). Thus compound Nos **17-20** were found to be active against *S. aureus*, *S. typhi*, *E. coli* and *A. tumefaciens* at 12.5-25.0 μg/ml. These four compounds also exhibited moderate antifungal activity against *T. mentagrophytes*, *M. canis* and *A. niger* at 12.5-25.0 μg/ml but were inactive against *C. albicans*. None of these compounds showed any significant antituberculosis activity.

Acknowledgement

The authors wish to thank Dr. G. S. Reddi and his staff of this department for antimicrobial screening and Mr. Shridhar Rao for technical assistance. They also thank the staff of analytical laboratories for elemental analyses and IR spectral data.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1121-1122

Analysis of Garlic for Its Metal Contents

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Manuscript received 30 January 1979, revised 28 April 1980, accepted 26 July 1980

Garlic in addition to being a condiment is claimed to have many medicinal properties. Since it is consumed in large quantities the content of metals were analysed which include Zn, Ni, Co, Cr, Fe, Ca, Mg, Cu, K, Na, V, Mo, Ti and Ce and are presented as mg/100 g fresh weight.

GARLIC (*Allium sativum*-Liliaceae) is reported to have antibacterial, antifungal, hypotensive, hypocholesterolemic, antidiabetic, antiinflammatory, anticancer and pesticidal activities[1]. It is also claimed to be prophylactic in occupational and chronic lead poisoning[2,3]. The toxic and therapeutic value of some of the metal elements are convincingly clear from recent reports[4,5]. Contents of few of these metals from garlic were reported elsewhere[6-13]. In the present communication, we are reporting the contents of Zn, Ni, Co, Cr, Fe, Ca, Mg, Cu, K, Na, V, Mo, Ti and Ce.

Experimental

After procuring from the market, the cloves devoid of the scales were dried and ashed. 0.5 gram ash was digested under refluxed condensor with a mixture of (1 : 1) concentrated hydrochloric acid and nitric acid (AR) for two hours and finally centrifuged. The residue was again digested with (1 : 4) concentrated perchloric acid and hydrochloric acid (AR) for one hour and centrifuged. Both the mother liquors were mixed and finally diluted to 100 ml with 0.1*N* hydrochloric acid. This solution was used for the estimation of metals. A Varian model AA6 atomic absorption spectrophotometer was used for the estimation of Zn, Ni, Co, Cr, Fe, Mg and Cu. V, Ti, Mo and Ce were estimated colorimetrically[14-17] using Spekol spectrophotometer. Na, K and Ca were estimated with Elico flame photometer.

Results and Discussion

The data for the metal contents obtained from the present investigation are presented in Table 1. The present method for the trace determination of metals is more sensitive compared to the earlier one. In the present investigation the concentration of the metals estimated in the garlic has some discrepancies in values reported by others[6-13]. The variation may be due to the environmental condition, and the soil in which the plant is growing. The metals reported in the earlier reports by various workers are; Ni-4.2, Cr-Traces, Cu-0.92, Sr-38.2, Al-2.86 and Mn-Traces mg/100 g fresh weight[8]; Zn-13.8 to 28.9, Fe-98.3 to 263.9, Cu-5.7 to 7.7 and Mn-23.6 to 54.6 ppm in the leaves[9]; Se-0.30 g/100 g fresh weight[6]; Fe-10 to 20 mg/100 g dry weight[7]. Se-90.3 r/100 g fresh weight[10]; Mo-42.3 g/100 g fresh weight[11]; Ca-116 mg, Fe-6, Na-76, K-2112, Mg-36 mg/Lb[12] and Ca-18, Fe-1.5, Na-18 and K-373 mg/100 g edible portion[13]. It can be seen from Table 1 that highest amount of metal found was K (410.6 mg/100 g fresh weight) whereas, Na content is much less (8.487 mg/100 g fresh weight). Next to K garlic contains Mg in a higher amount (17.820 mg/100 g fresh weight). Next to Mg garlic contains Na. Zn is next in the descending order (3.961 mg/100 g fresh weight). Ca is less than Zn (2.687 mg/100 g fresh weight). Fe content also is too less (1.895 mg/100 g fresh weight). All other metals estimated are less than one milligram. Of these metals V and Ni have been found essential for animals, but their essentiality for men have not been proved[18].

Table 1—Metal Contents of Garlic

Sl. No.	Metal	mg/100 g F. Wt.*
1.	Zn	3.961
2.	Ni	0.048
3.	Co	0.028
4.	Cr	0.023
5.	Fe	1.895
6.	Ca	2.687
7.	Mg	17.820
8.	Cu	0.170
9.	K	410.600
10.	Na	8.487
11.	V	0.010
12.	Mo	0.001
13.	Ti	0.001
14.	Ce	Traces

* All the results are a mean of five determinations.

Of the various metals reported earlier the content of Sr (38.2 mg/100 g fresh weight[8]) is of great importance. Sr behaves like Ca and follows it into

biological systems. Sr as such is not of much significance to us and is a non-essential element. But radioactive Sr can be a health hazard. Radioactive Sr is becoming widespread in the biosphere as a result of fall out from atomic weapons tests. This Sr^{90} has a long biological residence time as well as a long physical half life. It is a beta emitter which follows Ca metabolically and gets deposited in bone. The radiation emitted could result in bone cancer or leukemia if the levels were to become sufficiently high. Garlic can be considered a potential higher plant accumulating Sr and this can lead to serious health hazard especially in the regions where the radioactive fallout is high in the soil in which the plant grows.

Acknowledgement

We are gratefully indebted to Prof. S. M. Sethna, Pro-Vice Chancellor, M. S. University, Baroda for his keen interest and encouragement in this work. We are thankful to Prof. S. K. Banerjee for the laboratory facilities. We are also indebted to Dr. A. K. Ganguly, Ex-Director, Chemical Group, Bhabha Atomic Research Centre, for providing the necessary facilities.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1123-1124

3-Oxo-5-Phenylimino-1,2,4-thiadiazolidine and Its Some Aryl Analogues

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Manuscript received 27 February 1980, accepted 7 August 1980

Certain 3-oxo-2-unsubstituted/aryl substituted-4-unsubstituted/aryl substituted-5-phenylimino-1,2,4-thiadiazolidines involving interaction of S-chloro-N-phenyl isothiocarbamoyl chloride and parent and mono- and di-aryl carbamides have been prepared. Their structural assignments have been made on the basis of certain chemical transformations and IR spectral analysis.

INTERACTION of S-chloro-N-phenyl isothiocarbamoyl chloride and certain thioamido group containing compounds leading to certain 5- and 6-membered heterocyclic compounds have been investigated[1-3]. It therefore appeared quite interesting to investigate the behaviour of this isothiocarbamoyl chloride towards carbamides. With this end in view the reactions of S-chloro-N-phenyl isothiocarbamoyl chloride and carbamides have been investigated and certain 3-oxo-5-phenylimino-1,2,4-thiadiazolidines(I) have been isolated which cannot be prepared by the usual ways. The present communication is the record of these investigations.

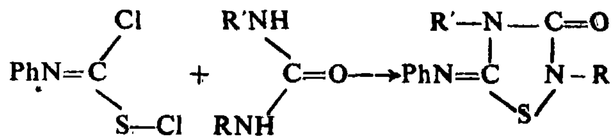
When the reaction of S-chloro-N-phenyl isothiocarbamoyl chloride and parent carbamide was carried out in boiling chloroform medium for 3 hr, evolution of hydrogen chloride was clearly observed. The insoluble solid was filtered and crystallised with aq. ethanol, m.p. 110°.

The product was assigned the structure 3-oxo-5-phenylimino-1,2,4-thiadiazolidine(Ia) on the basis of following facts :

The product was stable to boiling 8% alkali and also concentrated hydrochloric acid. It was not desulphurised when boiled with alkaline plumbite solution. On reaction with aniline in boiling ethanolic medium 1,3-diphenyl thiocarbamide, 152° and 1,3-diphenyl carbamide, 235° have been isolated. It was found stable to ethanolic ammoniacal hydrogen sulphide of moderate concentration. The IR spectrum of the product clearly indicated the presence of C=O, NH, C=N and C–S stretching frequencies.

When the reaction of this isothiocarbamoyl chloride has been extended to phenyl carbamide, 1,3-diphenyl carbamide, 1-phenyl-3-*p*-tolyl and 1-phenyl-3-*p*-Cl-phenyl carbamides, the related 1,2,4-thiadiazolidines(Ib-Ie) have been isolated. The structures of all these products have been assigned on the basis of usual chemical transformations and IR spectral analysis.

The formation of 1,2,4-thiadiazolidines may be represented as follows :



I

$$\text{I} + PhNH_2 \longrightarrow PhNH\text{—}\underset{\underset{S}{\|}}{C}\text{—}NHPh$$

$$+ RNH\text{—}\underset{\underset{O}{\|}}{C}\text{—}NHR'$$

where (a) R = R' = Hydrogen
(b) R = Phenyl and R' = Hydrogen
(c) R = R' = Phenyl
(d) R = Phenyl and R' = *p*-tolyl
(e) R = Phenyl and R' = *p*-Cl-Phenyl

S-chloro-N-phenyl isothiocarbamoyl chloride did not react with other mono- and di-aryl carbamides.

Experimental

The required S-Chloro-N-phenyl isothiocarbamoyl chloride was prepared by the usual procedure[1,5]. The parent carbamide used was of analytical grade. The mono-aryl and di-aryl carbamides were prepared by the interaction of aryl amines and carbamide and aryl amines and corresponding arylisothiocyanates, respectively.

Formation of 3-oxo-5-phenylimino-1,2,4-thiadiazolidine and the related compounds :

Details of a typical experiment (where R = R′ = Hydrogen) are as follow :

Carbamide (3.0 g) was suspended in chloroform (10 ml) and to this was added a chloroform solution of S-chloro-N-phenyl isothiocarbamoyl chloride (11.0 g). The reaction mixture was refluxed over a boiling water bath for 4 hr. During the reaction evolution of hydrogen chloride was noticed. The resultant solid was filtered and washed several times with chloroform followed by petroleum ether (3.2 g) and crystallised from aq. ethanol, m.p. 110° (Found : C 49.2, H 3.5, N 21.33, S 16.38. $C_8H_7N_3SO$ requires ; C 49.74, H 3.62, N 21.76, S 16.58%). It was identified as a 3-oxo-5-phenylimino-1,2,4-thiadiazoline(Ia) on the basis of following facts :

The product was stable to 8% boiling aq. alkali and conc. hydrochloric acid. It did not desulphurise when boiled with alkaline plumbite solution. On thermal decomposition the odours of phenylisothiocyanate and ammonia were quite perceptible. The product (1 g) on reaction with aniline (2 ml) in boiling ethanolic medium 1,3-diphenyl carbamide and 1,3-diphenyl carbamide, m.p. 152° and 235° respectively, have been isolated. The product could not be degraded with boiling alcoholic ammoniacal hydrogen sulphide of moderate concentration. IR spectrum of the product clearly indicated the presence of NH (3310 cm^{-1}), C=O (1660 cm^{-1}), C=N (1570 cm^{-1}), C—S (780 cm^{-1}) bands.

When the reaction of S-chloro-N-phenyl isothiocarbamoyl chloride was extended to phenyl carbamide, 1,3-diphenyl carbamide, 1-phenyl-3-*p*-tolyl and 1-phenyl-3-*p*-Cl-phenyl carbamides under the identical reaction conditions the related substituted 1,2,4-thiadiazolidines(Ib-Ie) have been isolated. These have been listed in Table 1.

TABLE 1—3-OXO-5-PHENYLIMINO-1,2,4-THIADIAZOLIDINE AND ITS ARYL SUBSTITUTED ANALOGUES

Reaction Conditions : Refluxing chloroform medium. S-Chloro-N-Phenyl isothiocarbamoyl chloride taken about 0.05 mole.

Sl. No.	Carbamide (g)	1,2,4-thiadiazolidine(I) (g, m.p. °C)	IR Characteristics (cm^{-1})
1.	Carbamide (3 g)	3-Oxo-5-phenylimino-(Ia) (2 g), 110°	NH (3310), C=O (1660), C=N (1570)
2.	Phenyl- (6 g)	3-Oxo-4-phenyl-5-phenylimino-(Ib), (5 g), 354°	NH (3340), C=O (1670), C=N (1620)
3.	1,3-Diphenyl- (10 g)	3-Oxo-2,4-diphenyl-5-phenylimino-(Ic),(13.2 g),345°	C=O (1660), C=N (1630)
4.	1-Phenyl-3-*p*-tolyl-(11g)	3-Oxo-2-phenyl-4-*p*-tolyl-5-phenylimino-(Id)(11.2 g),334°	C=O (1640), C=N (1560)
5.	1-Phenyl-3-*p*-Cl-phenyl-(11 g)	3-Oxo 2-*p*-Cl-phenyl-4-phenyl-5-phenylimino-(Ie) (14.5 g), 295°	C=O (1720), C=N (1640)

All the compounds exhibited consistent C, H, N and S analysis.

Acknowledgement

Authors are thankful to Dr. K. N. Munshi, Prof. and Head of the Department of Chemistry for providing necessary facilities.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1125-1128

Some 3-arylimino-5-(isopropylidene hydrazono-N)-1,2,4-dithiazolidines : Oxidative Debenzylation of 1-(isopropylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets

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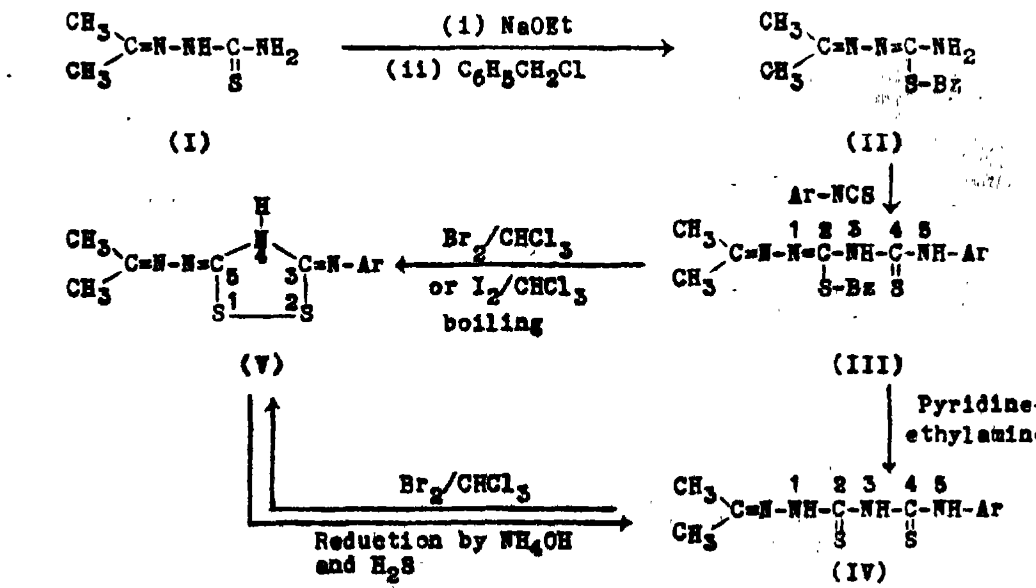
Manuscript received 30 November 1979, revised 30 May 1980, accepted 7 August 1980

The synthesis of 3-arylimino-5-(isopropylidenehydrazono-N)-1,2,4-dithiazolidines has been described by the oxidative debenzylation of the corresponding 1-(isopropylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets. These compounds have been characterized by the direct oxidation of the corresponding 2,4-dithiobiurets and also by i.r. spectra.

THE success of our investigations in the synthesis of 3, 5-disubstitutedimino-1, 2, 4-dithiazolidines through the oxidative dealkylation and cyclisation of the corresponding 1,5-disubstituted-2-S-alkyliso-4-thiobiurets[1-8] has convinced us about the feasibility of extending this reaction to the synthesis of some, hitherto, unknown 1,5-disubstituted-2-S-benzyliso-4-thiobiurets and their conversion to 3-arylimino-5-(isopropylidenehydrazono-N) - 1, 2, 4-dithiazolidines.

This communication describes the synthesis of certain new 3-arylimino-5-(isopropylidenehydrazono-N)-1,2,4-dithiazolidines by the oxidative debenzylation and ring closure of the related 1-(isopropylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets.

Acetonethiosemicarbazone(I) was benzylated with benzylchloride in ethanol in presence of sodium ethoxide, and resulting S-benzyliso-acetonethiosemicarbazone(II) was condensed with appropriate arylisothiocyanate to afford 1-(isopropylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets(III). The chloroform solution of the latter was then treated with bromine, when the benzyl group of these was eliminated as benzyl bromide followed by ring closure to the related 3-arylimino-5-(isopropylidenehydrazono-N)-1,2,4-dithiazolidines(V). These have also been obtained by the oxidation of the related



Where : Ar = Phenyl-, o-tolyl-, p-tolyl-, o-chlorophenyl-, p-chlorophenyl-, o-methoxyphenyl-, p-methoxyphenyl-, p-ethoxyphenyl.

*For Correspondence.

1-(isopropylideneamino)-5-aryl-2,4-dithiobiurets(IV), which were obtained by the reductive debenzylation of the related isodithiobiurets(III) with hydrogen sulphide in pyridine-triethylamine and also by the reduction of (V) under identical conditions. In all the cases, the structures of the compounds (IV) and (V) were confirmed by their synthesis through alternative routes as described above and also by mixed melting point technique and identical i.r. spectra.

The reactions have been represented :

Experimental

Melting points were determined by Kofler hot stage apparatus and are uncorrected.

TABLE 1—SYNTHESIS OF 1-(ISOPROPYLIDENEAMINO)-5-ARYL-2-S-BENZYLISO-4-THIOBIURETS(III)

Acetone-S-benzyl-isothiosemi-carbazone	Isothio-cyanates	1-(Isopropylidene-amino)-5-aryl-2-S-benzyliso-4-thio-biurets formed (Molecular formula)	m.p. °C	Yield
Acetone-S-benzyl-isothio-	Phenyl-	1-(Isopropylidene-amino)-5-phenyl- ($C_{18}H_{20}N_4S_2$)	215	62
Acetone-S-benzyl-isothio-	*o*-Tolyl-	1-(Isopropylidene-amino)-5-*o*-tolyl- ($C_{19}H_{22}N_4S_2$)	92	78
Acetone-S-benzyl-isothio-	*p*-Tolyl-	1-(Isopropylidene-amino)-5-*p*-tolyl- ($C_{19}H_{22}N_4S_2$)	146	80
Acetone-S-benzyl-isothio-	*o*-Chloro-phenyl-	1-(Isopropylidene-amino)-5-*o*-chloro-phenyl- ($C_{18}H_{19}N_4S_2Cl$)	182	70
Acetone-S-benzyl-isothio-	*p*-Chloro-phenyl-	1-(Isopropylidene-amino)-5-*p*-chloro-phenyl- ($C_{18}H_{19}N_4S_2Cl$)	185	85
Acetone-S-benzyl-isothio-	*o*-Methoxy-phenyl-	1-(Isopropylidene-amino)-5-*o*-methoxy-phenyl- ($C_{19}H_{22}N_4S_2O$)	180	82
Acetone-S-benzyl-isothio-	*p*-Methoxy-phenyl-	1-(Isopropylidene-amino)-5-*p*-methoxy-phenyl- ($C_{19}H_{22}N_4S_2O$)	161	82
Acetone-S-benzyl-isothio-	*p*-Ethoxy-phenyl-	1-(Isopropylidene-amino)-5-*p*-ethoxy-phenyl- ($C_{20}H_{24}N_4S_2O$)	182	85

Typical i.r. frequencies (cm^{-1}) of 1-(isopropylideneamino)-5-phenyl-2-S-benzyliso-4-thiobiuret : 3200m, N–H stretching ; 1120, 1145 vs, 1200 w, $N-\underset{\underset{S}{\|}}{C}-N$ grouping, 1590 w, $N-C=N-$ grouping.

All the compounds gave consistent C, H and N analyses.

Acetone thiosemicarbazone(I) was prepared by the known procedure[7] and its S-benzyl derivative (II) was obtained by benzylation with benzyl chloride in presence of sodium ethoxide[8].

1-(Isopropylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets(III) :

The details of a typical experiment are as follows :

Benzene solution of S-benzyliso acetonethiosemicarbazone (2.21 g) was refluxed with phenylisothiocyanate (1.35 g) for 1 hr. On evaporation of the solvent, 1-(isopropylideneamino)-5-phenyl-2-S-benzyliso-4-thiobiuret was obtained as a semisolid which on washing with petroleum ether and addition of a little ethanol became crystalline. It was crystallized from ethanol, m.p. 215° (yield 2.6 g, 70%). The results of these experiments are summarized in Table 1.

3-Arylimino-5-(isopropylidenehydrazono-N)-1,2,4-dithiazolidines(V) :

(i) Oxidative debenzylation of 1-(isopropylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets :

The substituted 2-S-benzyliso-4-thiobiuret made into a paste with a little chloroform or carbon tetrachloride was treated with liquid bromine until the colour of bromine persisted. The reaction mixture warmed up considerably evolving lachrymatory fumes of benzyl bromide. After 30 min, the semisolid product was washed first with ether and then with a mixture of ether and little ethanol, when the hydrobromide of the oxidation product separated out as a crystalline mass. On treatment with ammonia the free base was obtained, which was thoroughly washed with ether, and crystallized from ethanol. The dithiazolidine bases thus obtained showed no depression in m.p. when mixed with the authentic samples obtained by the oxidation of the corresponding 1,5-disubstituted-2,4-dithiobiurets.

(ii) Oxidation of 1-(isopropylideneamino)-5-aryl-2,4-dithiobiurets(IV) with bromine in ethanol :

The 1-(isopropylideneamino)-5-aryl-2,4-dithiobiurets listed in Table 3 were oxidized with bromine in dilute ethanolic solution and ether added when the hydrobromide of the respective 3-arylimino-5-(isopropylidenehydrazono-N) - 1, 2, 4-dithiazolidine precipitated. Free bases were obtained by treating these with ammonia and crystallized from ethanol (Table 2).

1-(Isopropylideneamino)-5-aryl-2,4-dithiobiurets (IV) :

(i) Reductive debenzylation of 1-(isopropylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets(III) :

TABLE 2—3-ARYLIMINO-5-(ISOPROPYLIDENEHYDRAZONO-N)-1,2,4-DITHIAZOLIDINES(V) : OXIDATIVE DEBENZYLATION OF 1-(ISOPROPYLIDENEAMINO)-5-ARYL-2-S-BENZYLISO-4-THIOBIURETS(III) WITH LIQUID BROMINE IN CHLOROFORM

1-(Isopropylidene-amino)-5-aryl-2-S-benzyliso-4-thiobiurets : oxidized	3-Arylimino-5-(isopropylidene hydrazono-N)-1,2,4-dithiazolidines : formed (Molecular formula)	m.p. °C	Yield
1-(Isopropylidene-amino)-5-phenyl-	3-phenylimino-5-(isopropylidenehydrazono-N)- ($C_{11}H_{12}N_4S_2$)	135	70
1-(Isopropylidene-amino)-5-*o*-tolyl-	3-*o*-tolylimino-5-(isopropylidenehydrazono-N)- ($C_{12}H_{14}N_4S_2$)	160	75
1-(Isopropylidene-amino)-5-*p*-tolyl-	3-*p*-tolylimino-5-(isopropylidenehydrazono-N)- ($C_{12}H_{14}N_4S_2$)	154	85
1-(Isopropylidene-amino)-5-*o*-chloro-phenyl-	3-*o*-chlorophenylimino-5-(isopropylidenehydrazono-N)- ($C_{11}H_{11}N_4S_2Cl$)	181	72
1-(Isopropylidene-amino)-5-*p*-chloro-phenyl-	3-*p*-chlorophenylimino-5-(isopropylidenehydrazono-N)- ($C_{11}H_{11}N_4S_2Cl$)	138	90
1-(Isopropylidene-amino)-5-*o*-methoxyphenyl-	3-*o*-methoxyphenylimino-5-(isopropylidenehydrazono-N)- ($C_{12}H_{14}N_4S_2O$)	172	60
1-(Isopropylidene-amino)-5-*p*-methoxyphenyl-	3-*p*-methoxyphenylimino-5-(isopropylidenehydrazono-N)- ($C_{12}H_{14}N_4S_2O$)	164	65
1-(Isopropylidene-amino)-5-*p*-ethoxy-phenyl-	3-*p*-ethoxyphenylimino-5-(isopropylidenehydrazono-N)- ($C_{13}H_{16}N_4S_2O$)	152	70

Typical i.r. frequencies (cm^{-1}) of 3-phenylimino-5-(isopropylidenehydrazono-N)-1,2,4-dithiazolidene : C=N 1620 s ; ring –S–S–linkage 480 s ; 3200m, N–H stretching.

All the compounds gave consistent C, H and N analyses.

The desired isodithiobiuret(III) was dissolved in pyridinetriethylamine (6 : 1) solution and a stream of dry hydrogen sulphide passed for 3 hrs. The resulting solution on filtration, cooling and neutralization with dilute hydrochloric acid afforded the expected dithiobiuret(IV). These were crystallized from ethanol (Table 3).

(ii) Reduction of 3-arylimino-5-(isopropylidenehydrazono-N)-1,2,4-dithiazolidines(V) by ethanolic ammoniacal hydrogen sulphide :

The dithiazolidines were dissolved in hot ethanolic ammoniacal hydrogen sulphide solution and a stream of hydrogen sulphide passed for 3 hrs. The clear solution on dilution with water or acidification afforded the related dithiobiurets. These were crystallized from ethanol.

TABLE 3—SYNTHESIS OF 1-(ISOPROPYLIDENEAMINO)-5-ARYL-2,4-DITHIOBIURETS(IV) BY REDUCTIVE DEBENZYLATION OF 1-(ISOPROPYLIDENEAMINO)-5-ARYL-2-S-BENZYLISO-4-THIOBIURETS(III) WITH HYDROGEN SULPHIDE IN PYRIDINE-TRIETHYLAMINE

1-(Isopropylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets : reduced	1-(Isopropylideneamino)-5-aryl-2,4-dithiobiurets : formed (Molecular formula)	m.p. °C	Yield %
1-(Isopropylideneamino)-5-phenyl-	1-(Isopropylideneamino)-5-phenyl- ($C_{11}H_{14}N_4S_2$)	163	60
1-(Isopropylideneamino)-5-*o*-tolyl-	1-(Isopropylideneamino)-5-*o*-tolyl ($C_{12}H_{16}N_4S_2$)	115	72
1-(Isopropylideneamino)-5-*p*-tolyl-	1-(Isopropylideneamino)-5-*p*-tolyl- ($C_{12}H_{16}N_4S_2$)	127	78
1-(Isopropylideneamino)-5-*o*-chlorophenyl-	1-(Isopropylideneamino)-5-*o*-chlorophenyl- ($C_{11}H_{13}N_4S_2Cl$)	138	70
1-(Isopropylideneamino)-5-*p*-chlorophenyl-	1-(Isopropylideneamino)-5-*p*-chlorophenyl- ($C_{11}H_{13}N_4S_2Cl$)	152	80
1-(Isopropylideneamino)-5-*o*-methoxyphenyl	1-(Isopropylideneamino)-5-*o*-methoxyphenyl- ($C_{12}H_{16}N_4S_2O$)	145	75
1-(Isopropylideneamino)-5-*p*-methoxyphenyl-	1-(Isopropylideneamino)-5-*p*-methoxyphenyl- ($C_{12}H_{16}N_4S_2O$)	125	75
1-(Isopropylideneamino)-5-*p*-ethoxyphenyl-	1-(Isopropylideneamino)-5-*p*-ethoxyphenyl- ($C_{13}H_{18}N_4S_2O$)	140	70

Typical i.r. frequencies (cm^{-1}) of 1-(isopropylideneamino)-5-phenyl-2,4-dithiobiuret : 3395 w, N–H–stretching ; 1150 m, shows $N-\underset{\underset{S}{\|}}{C}-N$ grouping ; 1620 s, C=N grouping.

All the compounds gave consistent C, H and N analyses.

The identity of each product was established by mixed m.p. technique with the authentic sample obtained by conventional reduction of the isodithiobiurets described in Table 3 and by identical i.r. spectra.

Acknowledgement

The authors are thankful to Prof. B. M. Shukla, Head, Department of Chemistry, B.H.U., for providing necessary laboratory facilities. Financial assistance from C.S.I.R., New Delhi, is also gratefully acknowledged by one of us (S.K.R.).

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NOTES

Alkali Metal Complexes : Mixed Ligand Complexes of Alkali Metal Salts of Some Organic Acids with Ethylenediamine

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Manuscript received 24 November 1978, accepted 7 August 1980

ETHYLENEDIAMINE (en) forms a number of stable adducts with certain alkali metals[1] and their crystal structure showed that in case of lithium, each ion is tetrahedrally surrounded by four nitrogen atoms from three ethylenediamine molecules[2]. So it was thought worthwhile to extend the investigation by a systematic examination, and in the present work, we are reporting the synthesis of a number of stable and soluble mixed ligand complexes of ethylenediamine with alkali metal salts of some organic acids.

Experimental

The usual method of preparation of all the metal salts of organic acids was same except that for metal salts of picolinic acid. The powdered salts were taken in a flask and benzene was added to it, the salts were insoluble in benzene. This suspension of salts in benzene was heated to boiling and ethylenediamine was added to it dropwise. The addition of ethylenediamine was continued till whole of the salt went into solution. After that the clear solution was evaporated at 110°. The heating was done very slowly and cautiously till almost whole of the liquid evaporated off. The crystals, thus obtained, were then scratched and washed with small amount of cold benzene and dried in an oven at a temperature of 100°. In the case of metal picolinates, the clear solution of benzene with M.PicA and ethylenediamine, were allowed to cool when white crystals separated out. These were filtered, washed with cold benzene and dried at a temperature of 100°.

Results and Discussion

All the complexes are stable in dry air. As the alkali metal complexes take up moisture and decompose due to hydrolysis, these complexes were kept in a desiccator over anhydrous $CaCl_2$. When the system is heated, a transformation at a temperature higher than the boiling point of ethylenediamine is produced. The colour, transition or decomposition temperatures and analysis of the complexes are given in Table 1.

The solubilisation of the alkali metal salts of these organic acids in benzene by the addition of ethylenediamine clearly shows that complexes are formed in solution. Covalency in these complexes

TABLE 1—SOME PROPERTIES AND ANALYTICAL DATA

Compound	Colour	Temperature	Found(%)				Calculated(%)			
			C	H	N	M	C	H	N	M
Li8HQ.en	Yellowish brown	240-244d	62.80	5.72	19.84	—	62.56	6.64	19.91	—
Na8HQ.en	Yellow	120d	58.80	6.40	18.66	10.00	58.15	6.17	18.50	10.13
K 8HQ.en	Olive	140-160d	58.85	5.80	16.88	16.00	54.22	5.76	17.28	16.05
NaONP.en	Red	160d	48.27	5.40	18.57	11.05	48.44	5.48	19.00	10.41
K ONP.en	Orange red	120-140d	39.90	4.67	17.15	16.80	40.51	5.06	17.72	16.46
LiPicA.en	White	170d	50.80	5.88	21.90	—	50.79	6.85	22.22	—
NaPicA.en	Pale yellow	248d	46.28	5.85	19.88	11.00	46.88	5.85	20.49	11.22
LiAnth.en	Light brown	235d	52.56	8.01	19.80	—	52.48	8.25	20.89	—
NaAnth.en	Light brown	240d	49.20	7.87	18.52	10.18	48.65	7.66	18.92	10.86
LiSalA.en	Pale yellow	205-210t	52.10	6.50	13.86	—	52.94	6.37	13.73	—
NaSalA.en	Light brown	240-245d	49.60	5.71	12.42	10.32	49.09	5.91	12.78	10.45
LiSalH.en	Yellow	140-145d	57.51	6.68	14.42	—	57.45	6.91	14.89	—
NaSalH.en	Yellow	115d	53.50	6.50	13.34	11.31	52.94	6.37	13.78	11.27
K SalH.en	Brown	240d	48.81	5.85	12.10	17.52	49.09	5.91	12.78	17.73
Na1N2N.en	Green	185d	55.91	5.07	16.90	9.02	56.47	5.49	16.47	9.02
K2H3NA.en	Light brown	220-225d	54.20	5.50	9.95	13.78	54.55	5.24	9.79	13.64

d = decomposition ; t = transition.
en = ethylenediamine ; 8HQ = 8-hydroxyquinoline ; ONP = *o*-nitrophenol ; PicA = picolinic acid ; Anth = anthranilic acid ; SalA = salicylic acid ; SalH = salicylaldehyde ; 1N2N = 1-nitroso-2-naphthol ; 2H3NA = 2-hydroxy-3-naphthoic acid.

is suggested on the basis that these are soluble in non-polar solvent benzene. That these adducts are genuine complexes and not stoichiometric mixtures is also clear from the fact that these complexes decompose at a temperature much higher than the boiling point of ethylenediamine. The complexes in absence of excess of ethylenediamine decompose in non-aqueous solvents, leaving the insoluble metal salts. As such conductivity values could not be ascertained.

An examination of the infrared spectra of alkali-metal-ethylenediamine complexes shows (Table 2)

TABLE 2—SELECTED IR ABSORPTION BANDS (cm^{-1})

Li8HQ.en		3390		3200	1610	1330	1020	810	795
KSalH.en		3370		3200	1605sh	1320	1030	820sh	810
LiSalA.en		3370		3180	1605	1295	1020	825	820
NaSalA.en		3360		3200	1600sh	1320	1025	810	800sh
LiAnth.en		3380		3270	1610	1320	1026	822	800
NaAnth.en	3450	3400	3340				1040	825	820sh

sh = shoulder.

that different NH_2 vibrations are present in the complexes ; though in some cases the vibrations of the acid-salts of alkali metals overlap the NH_2 vibrations. When these frequencies are compared with those obtained for Zn, Cd and Hg[3], there seems no doubt, that *en* group in all these compounds has the same configuration.

The two N – H stretching vibrations appear as medium peaks between 3400-3200 cm^{-1}. The 3377 cm^{-1} peak of ethylenediamine remains unaffected after complexation, but the 3316 cm^{-1} peak is very much affected in the complexes. This appears at 3200 cm^{-1} with reduced intensity in the complexes thereby suggesting that there has been decrease in the bond order of N – H on complexation. The NH_2 bend vibration can be located as a single sharp peak (or shoulder) at 1605 cm^{-1} region. The ligand vibrations of the acid-salts very much interfere with the NH_2 bend vibrations. The NH_2 wag and twist appear at 1320 and 1020 cm^{-1} region as weak or medium peak.

On comparing the vibrations of NH_2 in ethylenediamine in alkali-metal salt-ethylenediamine complexes with that of 'standards'[4] whose structures are already known, it is suggested that, because of the similarity and simpleness of the spectra, ethylenediamine has a bridging *trans*-structure.

Further to have more evidence regarding the *trans*-structure, the CH_2 rocking region 870-900 cm^{-1}, were also looked into. In all the complexes two peaks appeared between 820-800 cm^{-1}, which further points to *trans*-structure[5].

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Studies on Vanadium (V)-N-*m*-Tolyl-*p*-Methoxy-Benzohydroxamic Acid Complex

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Manuscript received 30 June 1979, revised 23 July 1980, accepted 7 August 1980

N-*m*-TOLYL-*p*-METHOXYBENZOHYDROXAMIC acid (TMBHA) has been used for the spectrophotometric determination of vanadium(V) by solvent extraction technique[1]. The present paper deals with the determination of dissociation constant of the reagent (TMBHA) from the extraction data analysis and evaluation of the stepwise stability constants of its complex with vanadium(V). The Yatsimirskii's[2,3] and Leden's[4] graphical extrapolation methods were applied with necessary modification[5] to calculate the values of stepwise stability constants. The overall stability constants of the complex also have been determined by Job's[6] and Harvey and Manning's[7] methods.

Experimental

Reagent and solutions : A stock solution of V(V) was prepared by dissolving vanadium pentoxide (A.R. ; B.D.H.) in dilute hydrochloric acid and the vanadium content was determined by standard methods[8].

N-*m*-Tolyl-*p*-methoxybenzohydroxamic acid (TMBHA) was synthesised by known methods[9]. A fresh solution of the reagent was prepared in pure chloroform.

Apparatus : An ELICO *p*H meter with glass and saturated calomel electrode was employed for *p*H adjustments. Beckman DU2 spectrophotometer with quartz cells of 1.00 cm light path was used for all photometric measurements. All measurements were made at 30° ± 1°.

General Procedure : An aliquot of the vanadium(V) solution was taken and to it added enough concentrated hydrochloric acid so as to make acid strength about 4.0 *M*. Total volume of the aqueous phase was made upto 10 ml with double distilled

water and equilibrated with 10 ml of the reagent solution in chloroform. After equilibration, two phases were separated and the absorbance of the extracted violet coloured vanadium complex was noted at 530 nm against similarly processed reagent solution as a blank. The vanadium extracted was computed from the appropriate calibration curve.

Results and Discussion

Absorption spectra of TMBHA : The absorption spectrum of the TMBHA solution in chloroform against the pure chloroform blank shows maximum absorbance at 255 nm. The molar absorptivity of the reagent at 255 nm is 1.50×10^4. The reagent follows Beer's law in the concentration range of $0.33 - 15.0 \times 10^{-5}$ *M* in chloroform at 255 nm.

Distribution of reagent : A 10 ml solution of the reagent, HR, of known concentration, $[HR]_{tot}$ in chloroform was equilibrated with equal volume of aqueous solution at *p*H 1.0-12.0 and ionic strength of 0.2 *M* as maintained by $NaClO_4$. The concentration of the reagent in organic phase, $[HR]_{org}$ was determined by noting the absorbance of the solution at 255 nm against the similarly processed chloroform as a blank and reading from the calibration curve. The distribution of reagent, (D_R) is then :

$$D_R = [HR]_{org}/[HR]_{tot} - [HR]_{org}$$

The results obtained from the distribution study of TMBHA in chloroform-water system are incorporated in Fig. 1. The distribution decreases above *p*H 10.0 which may be attributed to the dissociation of the proton from =NOH group of TMBHA.

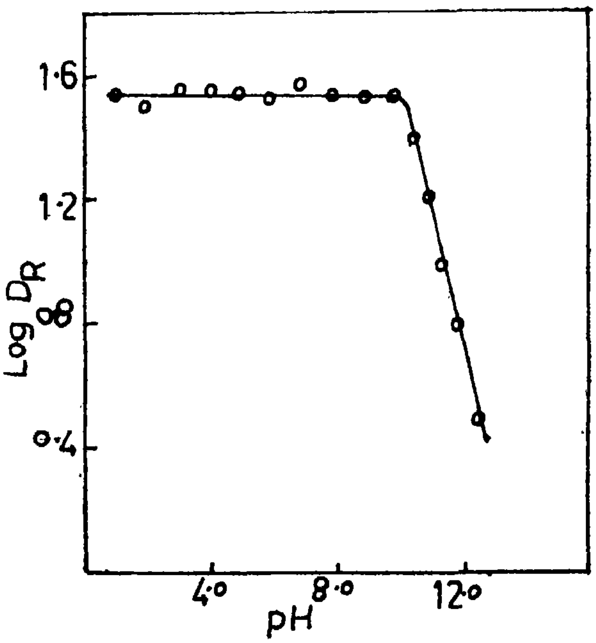


Fig. 1. Distribution of reagent as a function of *p*H.

Proton-ligand stability constants : If K_1^H is the proton-ligand association constant, P_R the partition constant of reagent HR, then the distribution ratio may be given as[10]

$$\frac{1}{D_R} = \frac{1}{P_R}\left(1 + \frac{1}{K_1^H.[H^+]}\right) \quad \ldots \quad (1)$$

At low *p*H, $D_R = P_R$. Thus, Fig. 1 gives the value of log P_R. The log P_R for TMBHA between chloroform and water is found to be 1.54. The negative slope region of Fig. 1 holds the relation

$$\log \frac{(P_R - D_R)}{D_R} = pH - \log K_1^H$$

This gives the value of log K_1^H (10.85) for TMBHA (Fig. 2). The value of log K_1^H was also found and compared by potentiometric[11] (10.91) and spectrophotometric[8] (11.20) methods. The values as found by various methods agree well with each other.

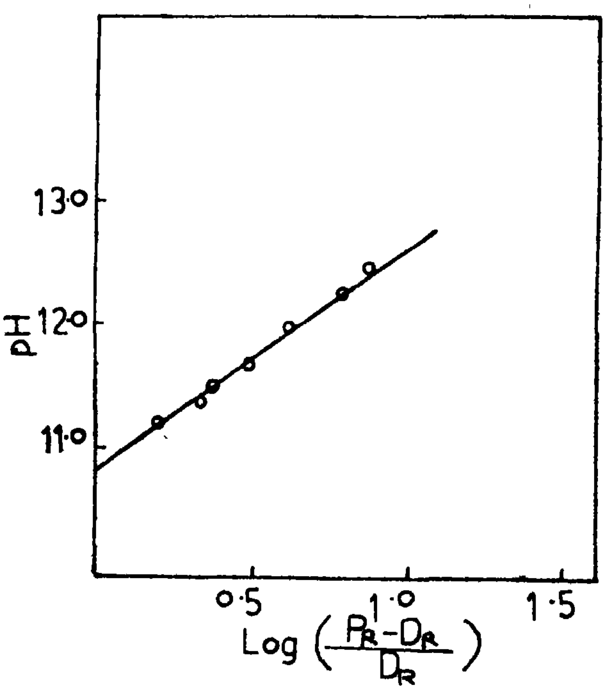


Fig. 2. $\log \frac{P_R - D_R}{D_R}$ as function of *p*H.

Composition and formation constants of the complex :

The composition studies of the extractable V(V)-TMBHA complex have been made by earlier workers[1]. The studies reveal that vanadium forms 1 : 2 (metal : ligand) complex with TMBHA in strong hydrochloric acid medium.

Stepwise formation constants for 1 : 2 system was calculated following Yatsimirskii's[4,5] and

Leden's[4] methods. The equilibrium ligand concentrations and the degree of complex formation were calculated from Beer's law data. The various functions were constructed and evaluated in the manner stated earlier[8].

The overall stability constant of the complex was determined by Job's[6] method and Harvey and Manning's[7] method. The values of stability constants as evaluated by various methods are compiled in the Table 1.

TABLE 1—STABILITY CONSTANTS FOR V(V)-TMBHA COMPLEX AT 30±1°C

Method	log K_1	log K_2	log β_2
Yatsimirskii's	5.11	4.68	9.79
Leden's	4.93	4.64	9.57
Job's	—	—	9.50
Harvey-Manning's	—	—	9.42

It seems from Table 1 that, the overall conditional metal-ligand stability constants as well as stepwise stability constants obtained by various methods agree well with each other.

Acknowledgement

Thanks are due to Council of Scientific and Industrial Research, India, for financial assistance.

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Spectrophotometric Studies of Lanthanide Complexes with 1-(2-Pyridylazo)-2-Naphthol(PAN) in Water-Ethanol Medium

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Manuscript received 18 June 1979, revised 22 May 1980, accepted 7 August 1980

SEVERAL reports have appeared in the literature on the studies of the formation of rare earth metal complexes with 1-(2-pyridylazo)-2-naphthol(PAN) and their extraction from aqueous solution into various organic solvents[1-10]. However, conflicting reports appeared in the literature regarding the composition of the extracted species, for example, Shibata[8] reported a composition of 1 : 2 Navrátil[4] 1 : 4 while Chang Tiao-Hsu and co-workers[6] reported a composition of 1 : 3. We described in our earlier communications[11,12] detailed solvent extraction characteristics and the preparation of lanthanide-PAN complexes in solid state and proposed an octahedral structure with a metal-ligand ratio of 1 : 3. In continuation of our earlier studies, we are now incorporating in this communication the results of our spectrophotometric study of these complexes in water-ethanol medium.

Experimental

Photometric measurements were carried out on Unicam SP 600 spectrophotometer and Spekol spectrocolorimeter using 1 cm corex cells. A Toshniwal Digital (Model CL 46) *p*H meter with a combined calomel-glass electrode was used for *p*H measurements.

Stock solutions of lanthanide metals were prepared by dissolving appropriate amounts of pure oxides (Apachae Chemicals, USA or E. Merck, Germany) in perchloric acid. The solutions were standardised with a standard solution of EDTA using xylenol orange as indicator[13].

1-(2-Pyridylazo)-2-naphthol(Riedel) was recrystallised from ethanol. A stock solution was prepared by dissolving 0.2493 gm of the dye in 100 ml of ethanol. Its strength was checked up by a photometric titration[14].

Ammonium hydroxide and ammonium chloride buffers were prepared in the *p*H range 8-10. All other chemicals used were of AnalaR or chemically pure grade. All experiments were carried out at room temperature (28±1°) and the ionic strength was maintained at 0.1±0.01 with NH_4Cl-NH_4OH buffer.

Recommended procedure for the photometric determination :

To an aliquot of the test solution containing (1-6 ml of 3×10^{-4} *M*) rare earth metal ion in a

25 ml volumetric flask, 5.0 ml of 3×10^{-4} *M* PAN in ethanol and 10 ml of NH_4Cl-NH_4OH buffer solution of *p*H 9.0 were added. The contents were thoroughly mixed and the total volume was made up to the mark with deionised water. The absorbance of the solution was then measured at 580 nm against reagent blank within 30 minutes of colour development.

Results and Discussion

Experiments were carried out in water-ethanol mixture since the lanthanide-PAN complexes and the reagent (PAN) are insoluble in water. The optimum composition of ethanol was found to be 20% (volume/volume). In 20% ethanol-water medium, the complex formation was found to be instantaneous and the intensity of the red colour was stable upto 30 minutes. However the solutions were found to develop turbidity on further standing.

The absorption spectra of all the lanthanide-PAN complexes in 20% ethanol-water medium at *p*H 9.0 showed well defined maxima at 580 nm while the reagent has no appreciable absorbance in this region.

It was found that lanthanides do not form complexes with PAN below *p*H 6.0. The optimum *p*H for complex formation was found to be 8-10. Ammonium chloride-Ammonium hydroxide buffers were found to be suitable and convenient to use in this *p*H range. The optimum *p*H range for maximum colour development for individual lanthanide complexes is shown in Table 1.

TABLE 1—pH RANGE, SPECTRAL PROPERTIES AND CONDITIONAL STABILITY CONSTANTS OF LANTHANIDE—PAN COMPLEXES

Temperature = 28±1°C   Ionic Strength = 0.10±0.01

Metal M^{3+}	*p*H range	λ_{max} nm	Beer's law limit, ppm	Molar extinction coefficient $\times10^{-4}$ moles^{-1}.lit.cm^{-1}	Conditional stability constant, log K'_f
Sm	7.5- 9.5	580	1.44	4.79	18.71
Eu	8.5- 9.5	580	1.46	4.79	18.84
Gd	7.5- 9.5	580	1.18	5.14	15.27
Tb	8.5- 9.5	580	1.14	5.18	15.20
Dy	7.5- 9.5	580	1.17	5.08	15.21
Ho	7.5- 9.5	580	1.20	5.27	15.80
Er	7.5-10.0	580	1.20	5.42	15.47
Tm	8.0- 9.5	580	1.22	5.02	15.88
Yb	7.5- 9.5	580	1.25	5.05	15.27
Lu	8.5-10.0	580	1.26	5.20	15.84

The variation of PAN concentration at *p*H 9.0 revealed that maximum colour development was obtained when 10-15 fold excess of reagent to that of metal was present in the solution.

Under the optimum experimental conditions the lanthanide-PAN complexes obey Beer's law. The Beer's law limits for individual metals and molar extinction coefficient values are given in Table 1.

The study of interference of various foreign substances that commonly associate with lanthanides revealed that anions such as Cl^-, NO_3^-, SO_4^{2-}, CH_3COO^-, ClO_4^-, $C_2O_4^{2-}$ have no effect on the photometric estimation even when present in 1000 fold excess to that of the lanthanide ions. $P_2O_7^{4-}$ and F^- do not interfere with the colour formation if they are present in less than 10 fold excess. However PO_4^{3-}, EDTA, citrate and tartrate seriously interfere with the colour development even at equal concentrations to that of the lanthanides.

Ca(II), Mg(II), Cr(VI), Mo(VI) and Tl(I) do not interfere with the photometric estimation when present in 100 fold excess. Be(II), Al(III), Zr(IV), Th(IV) and V(V) do not interfere with the determination when present in less than 10 fold and in presence of excess of the reagent (PAN). However, Fe(III), Ni(II), Cu(II), Zn(II), Cd(II) and U(VI) interfere seriously with the photometric estimation as these ions are known to form coloured complexes with PAN under experimental conditions.

Composition and Stability constants :

Investigations of Coleman, Varga and Mastin[14] plots with the variation of *p*H and PAN concentration conclusively indicated the existence of only single absorbing species under the experimental conditions. Job's method of continuous variation[16] at *p*H 9.0 and in 20% water-ethanol medium showed a metal-ligand ratio of 1 : 3 in all the lanthanide-PAN complexes confirming our earlier interpretation of MR_3 type of complexes with an octahedral structure where PAN is acting as bidentate ligand[11,12].

The conditional stability constants of the lanthanide-PAN complexes were calculated by Likussar and Boltz[17] method using the expression

$$\log K'_f = 0.3750 - 3 \log k + \log y_{max} - 4 \log (1 - y_{max})$$

where K'_f is the conditional formation or stability constant of the complex, k is the sum of the total concentrations of the metal and reagent and the y_{max} is the value obtained from the normalised curve. The results of stability constants for individual lanthanide-PAN complexes were shown in Table 1.

Acknowledgement

The authors wish to thank M/s Apachae Chemicals (USA) and E. Merck (Germany) for providing rare earth oxides as gift. They are also thankful to Prof. M. N. Sastri for his keen interest and encouragement. One of us (I. M. Rao) thanks CSIR,

New Delhi for the award of a Senior Research Fellowship.

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Effect of Aluminium Sulfate on Potassium Release and *p*H of Kaolinite Type Tea Soils

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Manuscript received 29 July 1978, revised 24 March 1980, accepted 9 July 1980

CHENARY[1] reported that aluminium is well assimilated by the calcifirgedtea plants. The productivity of tea soils are being maintained by the supply of essential nutrients like nitrogen, potassium, phosphorous etc and every year 1000 kg crop of tea removed 20 kg/ha of potassium[2,3]. It has been found that a thirteen year old tea bush utilizes 900 kg of potash per hectare every year[4]. This laboratory study attempts to see the availability of inherent potassium, in soil as effected by application of hydrated aluminium sulfate. Where symptoms of K-deficiency are apparent on the tea bushes top dressings ranging from 200 to 400 kg/ha of muriate or sulfate of potash are suggested according to severity of symptoms. Further the study also envisages on the *p*H effect of aluminium sulfate[5].

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Experimental

Air-dried soil samples of specifications given in Table 1 was made to pass through a 100-mesh B.S. sieve and then five grams of soil was taken in aspirator bottles. The outlet of the bottles were closed with pure glasswool so that only clear supernatant solution could be taken out at pleasure. The soils were then treated with varying concentration eg. 0, 21, 63, 105 and 147 mg per 5 g soil, of BDH laboratory grade aluminium sulfate $Al_2(SO_4)_3 \cdot 16\,H_2O$. Exchange reactions were allowed to continue at room temperature (28°) for 28 hours. The supernatant solutions were then drained out and replaced with fresh solutions of aluminium sulfate as used at 28°. Again exchange reactions were allowed to continue for 24 hours in a thermostatic waterbath controlled at 44°. The same experiment was repeated at 55°.

TABLE 1—PHYSICO-CHEMICAL PROPERTIES OF THE SOIL USED IN THE PRESENT STUDY

Place—Jorhat (Tocklai) 26° 47′ N
Depth—0-30 cm.

(A) Aggregate analysis

Grain Size	% on a dry wt. basis
>5 mm	0.44
5-2 mm	2.38
2-1 mm	1.66
1-0.5 mm	3.43
0.5-0.25 mm	6.43
Total	14.29

(B) Mechanical Analysis (Universal Pippett Method, Piper[10])

Texture	Size (mm)	% on dry wt. basis
Coarse Sand	2.000	7.55
Fine Sand	0 200	44.70
Silt	0.020	40.00
Clay	0.002	7.50

(C) Nitrogen, Carbon, Potash, Phosphate content and C/N ratio and loss on ignition analysis.

(i)		(ii)	
Total – K_2O	7.4 $\times 10^3$ ppm	%N	0.108
Available – K_2O	0.09 $\times 10^3$ ppm	%Org.C	0.976
Total – P_2O_5	0.404 $\times 10^3$ ppm	%Loss of Ignition	3.55
Available – P_2O_5	0.004 $\times 10^3$ ppm	C/N Ratio	9.00

The *p*H of the extracted solutions were measured in an ELICO LI IO T *p*H Meter. The concentration of potassium in solution was estimated by Atomic Absorption Spectrophotometry (Beckman 1233).

Results and Discussion

It has been found in the above study that application of aluminium sulfate to the soils lead to a

lowering in pH value of the soil solution. It is also seen from Table 2 that the rate of lowering in pH is

TABLE 2—VARIATION IN pH AND POTASH RELEASE DUE TO APPLIED ALUMINIUM SULFATE AT DIFFERENT TEMPERATURE

Temperature	28°C		44°C		55°C	
Al-sulfate per 5 g soil mg	pH	ppm K_2O $\times 10^3$	pH	ppm K_2O $\times 10^3$	pH	ppm K_2O $\times 10^3$
0	10.10	2.29	10.05	1.68	9.70	1.36
21	9.90	2.66	9.80	1.95	8.80	1.66
63	9.50	3.10	8.75	2.76	6.75	2.77
105	9.30	3.81	8.05	3.76	4.20	3.95
147	8.10	5.62	5.90	5.48	3.90	4.32

enhanced by a rise in temperature. Fig. 1 depicts the changes in potassium release as effected by pH at three different temperatures namely, 28°, 44° and 55°. Fig. 2 and Table 3 show that the potassium supplying power of the soils increases with more and more additions of aluminium sulfate, in other words more potassium(K^+) ions are released from the exchange sites. Besides, with rise in temperature the rate of release is still higher. The order and molecularity of the rate processes can be determined by undertaking kinetic studies. This means that at normal temperature K^+ which is not available in the soil solution is made available at an increased temperature and this is further favoured by application of aluminium sulfate.

The fact that aluminium sulfate application lowers the pH of soil solution confirms the findings of Hsu and Bates[5]. They found that verniculite treated with hydroxy aluminium solutions in the

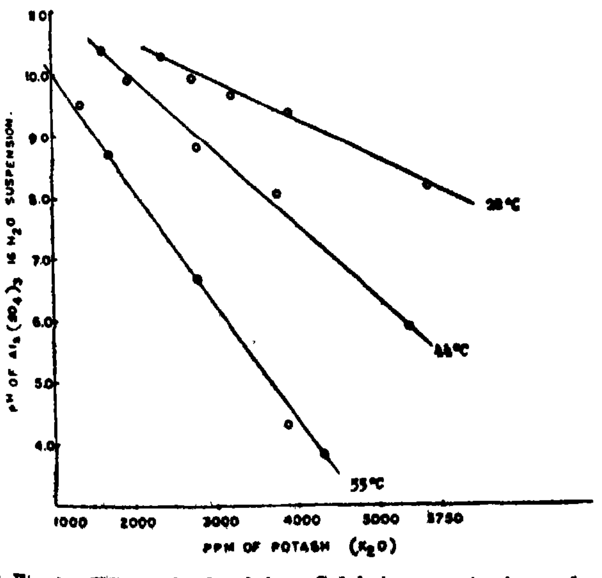


Fig. 1. Effect of Aluminium Sulphate on potassium release from tea soils at variable temperatures.

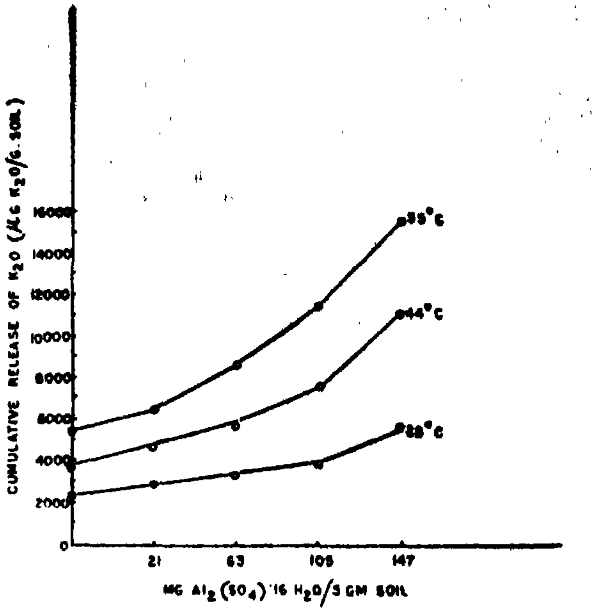


Fig. 2. Relationship between cumulative yield of Potash and Aluminium Sulphate applied.

TABLE 3—CUMULATIVE RELEASE OF POTASH WITH TEMPERATURE AT DIFFERENT CONCEN. OF AL-SULFATE TREATMENT

Al-sulfate per 5 g soil mg	Cumulative release of K_2O ppm $\times 10^3$ 28°C	44°C	55°C
0	2.29	3.87	5.23
21	2.66	4.61	6.27
63	3.10	5.86	8.63
104	3.81	7.58	11.58
147	5.62	11.04	15.36

range of NaOH/Al=0.3 to 1.2 showed on ageing a lowering in pH value as compared to the original solution.

The mechanism of the reaction is nothing but hydrolysis of the aluminium ions. First OH-Al polymer was formed and this enters into the lattices of the clay mineral. The Al in its turn enters into exchange reaction with the K^+ ions which get released to the soil solutions.

The process continues until the pH becomes so low that further hydrolysis of Al^{+3} is stopped. Evidently the magnitude of lowering will depend on the concentration of Al^{+3} ion in solution.

The phenomenon can also be explained by the following sets of reactions.

$$Al_2(SO_4)_3 = 2Al^{+3} + 3SO_4^{-2} \quad \ldots (1)$$

$$Al^{+3} + H_2O = Al(OH)^{+2} + H^+ \quad \ldots (2)$$

$$H_2O + H^+ = H_3O^+ \quad \ldots (3)$$

$$H_3O^+ + SO_4^{-2} = H_2SO_4 + H^+ \quad \ldots (4)$$

The reactions (1) and (2) show the hydrolysis of aluminium sulfate leading to the formation of $Al(OH)^{+2}$ which can undergo polymerisation. The reaction (3) is nothing but protonation of a water molecule which in its turn leads to the reaction (4). Brady[6], Black[7] are of the opinion that the Al^{+3} formed in reaction (1) can be absorbed on the surface of soil micelle and consequently lead to exchange reaction. From the kinetic standpoint it is expected that an increasing temperature would favour the forward reactions and evidently this is clear from the data in Table 2. It is expected that for each Al^{+3} ion there shall be three exchanged K^+ ion under ideal conditions.

Again a rise in temperature accelerates the rate of exchange reaction leading to more release of K^+ from the soil matrix. It is seen that at 28° the ammonium acetate exchangeable[8,10] potassium is only 0.57×10^2 ppm whereas after treatment with 21 mg of aluminium sulfate the soil solution contained 3.66×10^2 ppm of potassium. It has been reported that mature tea leaves contain about 1.7% aluminium, so toxic effect due to application of aluminium sulfate is far more remote[1,9]. However there must be a critical limit upto which we can apply aluminium sulfate so that it will not interfere with uptake of phosphorous by the plant.

Acknowledgement

The author acknowledges the Director, Tea Research Association and Head, Department of Soils and Meteorology, Tocklai Experimental Station for extending the laboratory facilities and for permission to publish this work. I also personally thank Miss Deepa Saikia for her help in course of this work. Above all, the author is deeply thankful to Prof. N. R. Dhar, Director, Sheila Dhar Institute of Soil Science, Allahabad, for his useful suggestions and constructive criticism.

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Synthesis of 4-[5-(4-Methyl-2-Phenylthiazolyl)]-2-Thiazolylhydrazones of Different Carbonyl Compounds

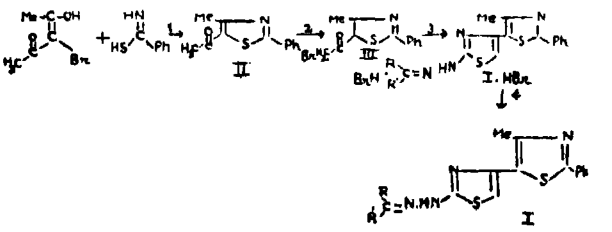
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Manuscript received 23 April 1979, revised 7 April 1980, accepted 7 August 1980

RECENTLY, Sawhney *et al* have reported the synthesis of differently substituted bithiazolyls as potential anti-inflammatory agents[1]. As many of these compounds exhibited significant anti-inflammatory activity, it was considered worthwhile to synthesise some analogous compounds. So, in continuation of our work on non-steroidal anti-inflammatory and anthel intic agents[2-6], we wish to report in the present communication the synthesis of 4-[5-(4-methyl-2-phenylthiazolyl)]-2-thiazolyl-hydrazones(I) of different carbonyl compounds with a view to testing their anti-inflammatory activity.

I were synthesised in excellent yields according to the reaction sequence outlined in Scheme 1.



Scheme—1

1. EtOH ; 2. $Br_2/CHCl_3$

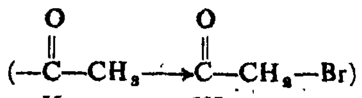
3. $\begin{matrix}R\\R'\end{matrix}\!\!>C=N.NH-\overset{S}{\overset{\|}{C}}-NH_2/_{EtOH}$ & 4. NH_4OH.

1-Acetyl-1-bromoacetone reacted smoothly with phenylthioamide in ethanol to give 5-acetyl-4-methyl-2-phenylthiazole(II)[7]. 5-Bromoacetyl-4-methyl-2-phenylthiazole(III) was obtained in good yield by the bromination of II with bromine in chloroform. III on condensation with different aldehyde and ketone thiosemicarbazones[8], which were prepared by treating the corresponding carbonyl compounds with thiosemicarbazide in presence of acetic acid, gave respective hydrobromide salts (I. HBr) of the required hydrazones(I). The corresponding free bases(I) could be easily obtained on neutralization of I. HBr with ammonia.

The structures of the final compounds as well as intermediates were confirmed by their elemental analysis and i.r. spectra. All the final compounds(I) absorbed in the region of 3400-3200 cm^{-1} (NH stretching) and 1620-1600 cm^{-1} (NH bending) did

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not show any absorption in the region of 1750-1650 cm^{-1} (absence of C=O). Replacement of hydrogen by bromine



II III

resulted in the expected shift of absorption frequency from 1680 cm^{-1} to 1690 cm^{-1}. The m.p.'s of II and III were also found to be identical with those reported earlier[7].

Selected compounds(I) have been sent for testing their anti-inflammatory activity.

Experimental

All the m.p.'s were taken in open capillaries in a sulphuric acid bath and are uncorrected. IR spectra were recorded for nujol mulls with IR-20 Spectrophotometer.

5-Acetyl-4-methyl-2-phenylthiazole(II) : It was prepared by treating 1-acetyl-1-bromoacetone with phenylthioamide using the literature procedure[7] and crystallized from methanol yield 66% m.p. 68° (lit. m.p. 67°) ; IR : 1680 cm^{-1} (C=O).

5-Bromoacetyl-4-methyl-2-phenylthiazole(III) : It was prepared by the bromination of II with bromine in dry chloroform following the method reported by us[3] for the bromination of 2-acetyl-1-methylbenzimidazole and crystallized from ethanol, yield 73% ; m.p. 115° (lit.[7] m.p. 116-17°) ; IR 1690 cm^{-1} (C=O).

General method for the preparation of required hydrazones(I) : A solution of aldehyde or ketone thiosemicarbazone[8] (0.01 mole) in ethanol (20 ml) was added to a solution of III (0.01 mole) in ethanol (30 ml) and the mixture was heated under reflux on a steam bath for about an hour. A brown-red crystalline solid separated out in hot solution. The solution of reaction mixture was cooled, collected by filtration, washed with a little ethanol and dried well to give pure I. HBr. This solid was suspended in water, neutralized with dilute ammonia, filtered, washed with water and then crystallized from a suitable solvent to give the required pure crystalline hydrazone(I). Purity of the compounds(I) was checked by tlc using silica gel G as adsorbent. Physical data of I are given in Table 1.

TABLE 1—PHYSICAL DATA OF I

Sl. No.	R	R[1]	m.p.[a] °C	Solvent of Crystallization	Yield %
1.	CH_3	CH_3	148-49[b]	D	60
2.	CH_3	Phenyl	91 (195)	A	63
3.	CH_3	4-Hydroxy-Phenyl	141 (233-35)	B	67
4.	CH_3	4-Methoxy-Phenyl	178 (208-09)	B	72
5.	CH_3	4-Nitro-Phenyl	243 (>250[c])	C	83
6.	CH_3	4-Amino-Phenyl	187-88[b]	B	61
7.	CH_3	4-Diethyl-aminophenyl	170[b]	B	71
8.	H	Phenyl	97 (217[c])	A	69
9.	H	4-Hydroxy-Phenyl	142 (206)	B	65
10.	H	4-Methoxy-Phenyl	178 (215-16)	A	77
11.	H	4-Hydroxy-2-methoxy-phenyl	122	B	70

a. The figures in bracket represent the melting points of hydrobromides (I. HBr)

b. The hydrobromides of these compounds could not be isolated.

c. Compounds melted with decomposition.

A : Ethanol, B : Toluene, C : Xylene, D : Dioxan/water.

Acknowledgement

Thanks are due to Head of the Chemistry Deptt., Meerut College, Meerut and Head of the Chemistry Deptt., University of Roorkee, Roorkee for providing the necessary research facilities.

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Synthesis and Antimicrobial Screening of 1,2-Benzisoxazolyl Schiff Bases

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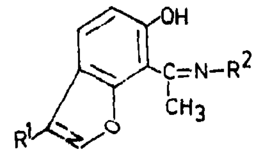
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Manuscript received 8 January 1979, revised 14 February 1980, accepted 9 August 1980

SCHIFF bases have gained importance because of the physiological and pharmacological activities associated with them. Schiff bases exhibit anticancer and antitubercular activity[1,2]. Anticancer Schiff bases have been prepared by the condensation of aniline with substituted benzaldehydes[3]. Isoxazolyl Schiff bases have been synthesised as possible antibacterial and antifungal agents[4].

In view of these important observations, some 1,2-benzisoxazolyl Schiff bases have been synthesised to study their antimicrobial activity. All the Schiff bases (I and II in Table 1) were prepared by the condensation of 7-acetyl-6-hydroxy-3-methyl and 7-acetyl-6-hydroxy-3-ethyl-1,2-benzisoxazoles[5] with several aromatic amines in presence of catalytic amount of piperidine in alcohol. The structures of these compounds were supported by elemental analyses and infrared spectroscopy.

TABLE 1—PHYSICAL DATA AND ANTITUBERCULAR ACTIVITY (in μg/ml) OF THE SCHIFF BASES (I AND II)



Sl. No.	Substituent R^2	m.p. °C	Yield %
	Compound I		
1.	Phenyl	128[a]	80
2.	2'-Methyl phenyl	155[a]	82
3.	4'-Methyl phenyl	148[b]	75
4.	3'-Methoxyphenyl	149[b]	69
5.	4'-Methoxyphenyl	176[b]	80
6.	3'-Chlorophenyl	142[b]	85
7.	4'-Chlorophenyl	166-68[b]	87
8.	4'-Bromophenyl	170[b]	83
9.	3'-Hydroxyphenyl	215[b]	68
10.	4'-Hydroxyphenyl	262[b]	85
	Compound II		
11.	Phenyl	94[b]	68
12.	2'-Methyl phenyl	142-3[b]	65
13.	4'-Methyl phenyl	95[c]	70
14.	2'-Methoxyphenyl	99[c]	72
15.	3'-Methoxyphenyl	100[c]	68
16.	4'-Methoxyphenyl	95[c]	75
17.	3'-Chlorophenyl	88[a]	71
18.	4'-Chlorophenyl	149[b]	75
19.	4'-Bromophenyl	166[a]	72
20.	3'-Hydroxyphenyl	215-16[b]	80
21.	4'-Hydroxyphenyl	203[b]	82

All compounds gave satisfactory C, H and N analyses

a = crystallised from methanol,
b = crystallised from ethanol,
c = crystallised from 80% ethanol.

Antimicrobial activity :

Some of the compounds were screened for antibacterial activity against *S. aureus*, *S. typhi* and *C. albicans*; but none of the compounds showed significant activity. The antitubercular screening of the compounds was carried out against *Micobacterium tuberculosis* ($H_{37}Rv$) by a Doub and Youmans' method[6]. Some of the compounds were found to be promising against *M. tuberculosis* (Table 1).

Acknowledgement

Authors are grateful to Dr. M. H. Shah, Asstt. Director, Haffkine Institute, Bombay, for screening the compounds for antimicrobial activity. One of the authors (A.B.D.) is thankful to CSIR, New Delhi, for the award of a Post-doctoral fellowship.

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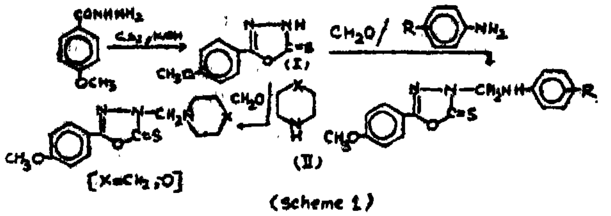
Synthesis of 5-(*p*-Methoxyphenyl)-1,3,4-Oxadiazole-2-thione Mannich Bases and Their Biological Evaluations

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Manuscript received 10 April 1980, revised 27 June 1980, accepted 7 August 1980

OXADIAZOLES have been associated with insecticidal[1,2], herbicidal[3], antibacterial[4,5], hypoglycemic[6], antitubercular[7], antiviral[8], antifungal[9] and carcinostatic[10] activities. Besides, 5-substituted-1,3,4-oxadiazole-2-thione yielded Mannich bases with primary aromatic amines[11]. It was therefore considered worthwhile to synthesise the title products incorporating the 1,3,4-oxadiazole-2-thione nucleus (Scheme 1) with a view to observe if such compounds could be of biological significance.



(Scheme 1)

Experimental

Melting points were determined in open capillaries and are uncorrected.

5-(p-Methoxyphenyl)-1,3,4-oxadiazole-2-thione(I) :

It was synthesised by following the reported method of Young and Wood[12] from *p*-methoxybenzoic acid hydrazide[13]. The resulting crude product was recrystallised from ethanol, m.p. 200° ; yield 80%.

Anal : Found : C, 51.20 ; H, 4.0 ; N, 13.5 ; $C_9H_8N_2O_2S$ requires C, 51.44 ; H, 3.84 ; N, 13.46%.

IR ; (cm^{-1}), 1610 (C=N), 1180 (C=S)

3-Arylaminomethyl-5-(p-methoxyphenyl)-1,3,4-oxadiazole-2-thiones(II) :

To a suspension[14] of I (2.08 g, 0.01 mole) in 15 ml ethanol, were added 40% formalin (0.75 ml, 0.01 mole) and aniline (0.94 g ; 0.01 mole). The reaction mixture was then warmed for 15 min on a water bath. It was then kept overnight. The product obtained was filtered and recrystallised from ethanol. Other such derivatives crystallised from alcohol and obtained in 70-90% yields are listed in Table 1.

The IR and NMR spectra of a typical compound *4* showed :

IR in KBr ; 3350 (NH), 1180 cm^{-1} (C=S)

NMR($CDCl_3$) δ ; OCH_3(Singlet) 3.78
$COOCH_3$(Singlet) 3.74
CH_2(Singlet) 5.4

Aromatic (Ar-H, Ar-NH-) multiplet 6.7-6.9 and 7.6-7.9.

Bio-Assay :

(A) *Insecticidal activity :*

The compounds in two concentrations[15] (0.5% and 0.1% in acetone) were injected in the 3/4 abdominal segment of the adult cockroaches with the help of a microsyringe. The tests were repeated and the control was done with parathione. The K. D. values of other derivatives(II) are given in Table 1.

Table 1—3-Arylaminomethyl-5-(p-methoxyphenyl)-1,3,4-oxadiazole-2-thione(II)

Sl. No.	Amines	m.p. °C	Insecticidal activity K.D. values (hrs) 0.5%	0.1%
1.	Piperidino	155	10	18.5
2.	Morpholino	166	12	14
3.	*p*-Carboxyanilino	258	9	18
4.	*p*-Carbomethoxyanilino	146	9.5	11
5.	*p*-Carbopropoxyanilino	150	10	18
6.	*p*-Carbobutoxyanilino	158	8.5	10.5
7.	*o*-Toluidino	180	10	14
8.	*m*-Toluidino	153-55	9	18.5
9.	*p*-Toluidino	148	10	18
10.	*o*-Carboxyanilino	231-32	9.5	14
11.	2,4-Dinitroanilino	174	8	12
12.	*p*-Anisidino	146	8	12.5
13.	*m*-Anisidino	186	9	18
14.	Anilino	186	10	15
15.	*p*-Chloroanilino	168	6	8.5
16.	*p*-Iodoanilino	191	10	12.5
	Acetone		36	
	Parathione		4	

The elemental analyses were found to be within satisfactory limits.

(B) *Antibacterial activity :*

The method, developed by Verma and Nobles[16] was employed for the determination of the antibacterial spectrum of I and other compounds of Table 1. The test organisms included *Staphylococcus aureus*, *Bacillus subtilis* and *Sorsena lutea*. The bacterial cultures maintained at the Public Analytical Laboratory, U.P. Government were used.

Results and Discussion

The parent oxadiazole(I) inhibited the growth of bacilli significantly but this activity was decreased in the Mannich bases derived from it except those containing a nitro group which inhibited only *S. aureus* and *S. lutea* to the corresponding value of (I). The insecticidal activity was, however, enhanced in the Mannich bases(II) and most significantly when there was incorporation of a chloro group.

Acknowledgement

The authors wish to thank Head of the Chemistry Department, Lucknow University for necessary Laboratory facilities. Grateful acknowledgement is made to the Director, Central Drug Research Institute for elemental analyses and spectra. One of them (K.K.P.) is indebted to the C.S.I.R., New Delhi, for a grant which defrayed part of the expenses of this work.

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Chemical Investigation of *Ochna squarrosa* Linn

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Manuscript received 27 November 1979, accepted 7 August 1980

OCHNA SQUARROSA Linn. (Ochnaceae) is a medicinally important plant used in Indian system of medicine for various diseases[1]. The earlier workers reported the presence of β-sitosterol from the plant[2]. In this communication we report three more known compounds-*n*-octacosanol, campesterol and β-sitosterol glycoside.

Experimental

Air dried powdered whole plant (2 kg) was successively extracted with petroleum ether (b.p. 60-80°), chloroform and methanol. The petrol extract was concentrated and column chromatographed over silica gel. On elution with hexane-benzene 1 : 1 mixture resulted in a colourless material which on crystallisation using hexane yielded a compound, m.p. 84°. This compound was identified as octacosanol by comparison with an authentic sample.

The chloroform extract was chromatographed over silica gel and on elution with benzene afforded white solid, m.p. 156° which on acetylation with acetic anhydride-pyridine furnished the corresponding acetate, m.p. 138° identical with an authentic specimen of campesterol acetate.

Further elution of the column with chloroform afforded a glycoside, m.p. 284° which on hydrolysis with methanolic hydrochloric acid gave an aglycone m.p. 136-37°, identical with an authentic sample of β-sitosterol. The sugar moiety after usual work up was identified as glucose, by paper chromatography. Finally the glycoside itself was compared with an authentic sample (m.p. and m.m.p.) and was found to be identical.

Acknowledgement

We thank Mrs. P. Brindha for the botanical identification of the plant and the Central Council for Research in Ayurveda and Siddha for their financial support.

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J. Indian Chem. Soc.,
Vol. LVII, November 1980, pp. 1141

Book Review

Stability Constants of Metal-Ion Complexes : Part B, Organic Ligands—Compiled by D. D. Perrin, Medical Chemistry Group, Institute of Advanced Studies, Australian National University, Canbera. **IUPAC Chemical Data Series No. 22** (International Union of Pure and Applied Chemistry, Analytical Chemistry Division, Commission on Equilibrium Data). Published by : Pergamon Press, Oxford, New York, Toronto, Sydney, Paris, Frankfurt.

This is an excellent compilation of stability constant data of metal-ion complexes with organic ligands published during the period, 1968-1973. Some data which were omitted from the Chemical Society Special Publication No. 17, 1964 and from the No. 25 1971, the first supplement to these tables, have been included in the Table of the present complilation. The errors in the earlier compilations have been corrected.

Stability constants on both binary and ternary systems appeared in almost all international and national journals on inorganic chemistry, analytical chemistry, biochemistry and in the abstracts of International and National symposia, conferences etc. on various aspects of these disciplines have been covered. The methods of measurement, temperature, solvent composition, ionic strength, back-ground electrolyte etc. and relevant chemical equations whenever required have been tabulated in the most systematic way. Changes in free energy, enthalpy and entropy associated with complex formation have also been recorded whenever such data were available. References of original literatures have been given with all the data.

It is an authentic dictionary of recent stability constant data and is an extremely useful ready source of such values and references to the inorganic chemists, analytical chemists, physical chemists, biochemists and bio-physicists.

The tables have been numbered by arranging the ligands on the basis of their chemical formulae following the Beilstein system of classification. IUPAC system of nomenclature has been followed in naming the ligands. The procedure for locating a particular table containing the stability constant data of a ligand of interest has been given at the beginning. The same table can also be approached from the chemical name index of the ligands given at the end. Any error in the tables and omission if there be any may be brought to the notice of the author for necessary corrections and inclusions. Author will also appreciate suggestions from users regarding inprovement of the tables.

G. N. Mukherjee

The Roussel Prize 1982

In view of the ever growing importance of steroids in therapeutic medicine, the late Mr. J. C. Roussel, Chairman of the well known French Pharmaceutical Company, created in 1968 an international Prize intended to stimulate further new research in this particular area.

The Prize is given every two years to a chemist or a biochemist whose work has been chosen as the most outstanding by an International Comittee of distinguished scientists in the field.

The preceding Roussel Prize were awarded :

- in 1970, to Pr. W. S. Johnson for his work on non-enzymatic biogenetic-like steroid synthesis,
- in 1972, to Pr. J. W. Cornforth for his work on enzymes of cholesterol biosynthesis,
- in 1974, to Pr. E. Kodicek and H. F. DeLuca for their work on metabolites and mechanism of action of cholecalciferol,
- in 1976, to Pr. E. E. Baulieu and E. V. Jensen for their work on hormone receptors,
- in 1978, to Pr. R. Breslow and G. Stork for their work of chemistry and synthesis in the steroid series,
- in 1980, to Pr. K. Arima and C. J. Sih for their work on the microbiological degradation of the sterol side chain.

The next Prize ($ 20.000) which is scheduled for April 1982 will be concerned with outstanding work on Chemistry and Biochemistry of Steroids and other squalenoids published before September 1st, 1981.

The composition of the Award Committee for the year 1982 is as follows -

President : Sir Derek Barton

Members : Pr. A. Crastes De Paulet, A. Eschenmoser, V. H. T. James, W. S. Johnson, L. Martini, K. Nakanishi

Secretary : Pr. J. Mathieu

Candidates for the Prize may be of any nationality and from any laboratory.

Nominations should be presented and supported by a personnality of high scientific level, on the appropriate form with the names of two referees, to the President or the Secretary of the Jury, before October 1st, 1981.

Forms and additional information are available from the Secretary on request.

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AUTHOR INDEX

J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1143-1146

Novel Reactions of Cobalt(II) Salts with Dibenzoylmethane and Nitrogen Donor Ligands

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Manuscript received 3 May 1980, revised 29 July 1980, accepted 9 September 1980

Reactions of cobaltous salts with dibenzoylmethane and nitrogen donor ligands in varied stoichiometric proportions resulted in the formation of a series of complexes of the type [Co X(bzbz)(H_2O)$_2$], [Co X(bzbz) L_2H_2O], [Co X(bzbz) L_2], [Co X(bzbz) L′(H_2O)$_2$], [Co X(bzbz)$_2$L], [Co(bzbz) L_2(H_2O)$_2$](ClO_4), [Co(bzbz) L″(H_2O)$_2$](ClO_4)$_2$ and [Co(NO_3)(bzbz)(H_2O)$_2$](where X = Cl^- or Br^-, bzbz.H = Dibenzoylmethane, L = Pyridine or substituted pyridine, L′ = Quinoline or Isoquinoline and L″ = 2,2′-bipyridine or 1, 10-phenanthroline). The compounds were characterised and possible stereochemistry deduced on the basis of analytical data, spectra (i. r. and electronic) conductivity and thermal decomposition studies. The compound having the composition [CoCl(bzbz)Py_2]exhibits penta coordination of divalent cobalt.

REACTION of cobaltous salt with dibenzoylmethane in alcoholic medium in 1 : 2 molar ratio results in the formation of diaquo *bis*-(dibenzoylmethanato) Cobalt(II) complex-Co(bzbz)$_2$(H_2O)$_2$- upon subsequent neutralisation with ammonia. Several mixed ligand complexes of Cobalt(II)[1,2], Cadmium(II)[3], Nickel(II)[4] and Zinc(II)[5,7] have been reported using ligands containing different donor atoms with varying electronegativities. It was therefore thought worthwhile to investigate the reaction of cobaltous salts with dibenzoylmethane in 1 : 1 stoichiometric ratio in presence of nitrogen donor ligands. In the present communication we report some penta- and hexa coordinated mixed ligand complexes of Cobalt(II) and Cobalt(III) obtained in the present investigation.

Experimental

All the chemicals were of Analar grade and the reactions were studied in absolute alcohol medium.

Preparation of mixed ligand complexes :

1. *[CoX(bzbz)(H_2O)$_2$] and [Co(NO_3)(bzbz)(H_2O)$_2$] :*

The compounds of this type were prepared by reacting the solutions of cobaltous salt and dibenzoylmethane in hot ethanol in exactly 1 : 1 molar ratio followed by dropwise addition of ammonia with vigorous shaking.

2. *[CoX(bzbz)L_2(H_2O)], [Co(bzbz)L_2(H_2O)$_2$](ClO_4) and [CoX(bzbz)L′(H_2O)$_2$] :*

These were obtained by adding slightly more amount of the ligand base than required for 1 : 2 ratio to the hot ethanolic solutions of cobaltous salt and dibenzoylmethane (in 1 : 1 ratio) and refluxing the contents for nearly an hour before neutralising the moderately hot solution with ammonia.

3. *[Co(bzbz)L″(H_2O)$_2$](ClO_4)$_2$:*

Cobalt perchlorate, dibenzoylmethane and the nitrogen donor ligand (bidentate) were taken in 1 : 1 : 1 molar ratio respectively and the contents were refluxed in ethanolic medium for 2 hours. Then the resulting solution was neutralised by adding ammonia with vigorous shaking.

4. *[CoX(bzbz)L_2] and [CoX(bzbz)$_2$L] :*

These were obtained by reacting Cobalt(II) salt and dibenzoylmethane in 1 : 1 and 1 : 2 molar ratio respectively in 200 ml of ethanol in presence of the excess of the ligand (1 : 3). The reaction mixture was kept under reflux for 1 hour. Then air was vigorously drawn through the solution for nearly two hours to get the desired product.

All the isolated complexes were filtered, washed with absolute alcohol several times to ensure complete removal of excess ligand, followed by ether and dried *in vacuo*.

Analyses :

Purity of the isolated compounds was established by estimating metal and halogen by standard methods. In some cases alkaline fusion was found necessary for estimating halogen. Conductance measurements were carried out in *M*/1000 acetone solution using Toshniwal conductivity bridge type CL 0102 with a dip type cell. The magnetic susceptibility measurements were carried out on solid specimen using Guoy method. Infrared spectra in the range 5000-200 cm^{-1} were recorded on nujol mull using Unicam SP-200, Perkin-Elmer and Beckman IR-12 spectrophotometers. The electronic spectra in the visible range were recorded on an Elico model CL 24 spectrophotometer. Thermogravimetric analyses were carried out in a manually

TABLE 1—ANALYSES, MOLAR CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA OF MIXED LIGAND COMPLEXES OF COBALT(II) AND COBALT(III)

Sl. No.	Compound	Colour	Cobalt(%) Found	Cobalt(%) Calc.	Halogen(%) Found	Halogen(%) Calc.	Λ_m (m hos)	μ_{eff} (B.M.)
1.	$[CoCl(bsbs)(H_2O)_2]$	Yellow	15.78	15.86	9.50	9.54	4.0	4.98
2.	$[CoBr(bsbs)(H_2O)_2]$	Orange yellow	14.14	14.19	19.18	19.24	3.5	4.91
3.	$[CoCl(bsbs)(Py)_2(H_2O)]$	Brick red	11.88	11.93	7.15	7.18	3.8	5.06
4.	$[CoBr(bsbs)(Py)_2(H_2O)]$	Orange yellow	10.90	10.95	14.88	14.84	3.5	4.99
5.*	$[CoCl(bsbs)(Py)_2]$	Orange red	12.36	12.39	7.40	7.45	3.5	4.82
6.	$[CoCl(bsbs)(\beta\text{-pic})_2(H_2O)]$	Dull yellow	11.22	11.30	6.75	6.80	4.6	5.04
7.	$[CoBr(bsbs)(\beta\text{-pic})_2(H_2O)]$	Orange yellow	10.37	10.41	14.02	14.11	3.5	4.91
8.	$[CoCl(bsbs)(\gamma\text{-pic})_2(H_2O)]$	Orange red	11.26	11.30	6.72	6.80	4.0	5.00
9.	$[CoBr(bsbs)(\gamma\text{-pic})_2(H_2O)]$	Dull orange red	10.38	10.41	14.05	14.11	4.2	4.95
10.°	$[CoCl(bsbs)_2(\gamma\text{-pic})]$	Orange red	9.28	9.30	5.52	5.59	5.8	Diamagnetic
11.	$[CoCl(bsbs)(Q)(H_2O)_2]$	Yellow	12.18	12.21	7.25	7.34	4.4	4.94
12.	$[CoBr(bsbs)(Q)(H_2O)_2]$	Yellow	11.14	11.18	15.08	15.16	3.8	4.96
13.	$[CoCl(bsbs)(IQ)(H_2O)_2]$	Yellow	12.16	12.21	7.28	7.34	3.0	5.08
14.	$[CoBr(bsbs)(IQ)(H_2O)_2]$	Orange yellow	11.15	11.18	15.06	15.16	2.7	5.02
15.	$[Co(NO_3)(bsbs)(H_2O)_2]$	Dull yellow	15.47	15.51	—	—	11.2	4.96
16.	$[Co(bsbs)(\gamma\text{-pic})_2(H_2O)_2](ClO_4)$	Yellow	9.70	9.76	5.75	5.87	140	5.20
17.°	$[Co(bsbs)(bipy)(H_2O)_2](ClO_4)_2$	Yellow	8.70	8.75	10.52	10.54	235	Diamagnetic
18.°	$[Co(bsbs)(Phen)(H_2O)_2](ClO_4)_2$	Orange red	8.58	8.68	10.35	10.40	232	Diamagnetic

* Coordination number is 5. In all other complexes, C.N. is 6.
° Valency of Cobalt is 3. In all other complexes, valency is 2.

TABLE 2—INFRARED (cm^{-1}) AND ELECTRONIC SPECTRAL DATA (nm) OF MIXED LIGAND COMPLEXES OF COBALT(II) AND COBALT(III)

Sl. No.	Compound	$\nu(C-O)$	$\nu(C-C)$	λ_{max} in (nm) ν_3	ν_2	ν_1
	Dibenzoylmethane	1600s	1553			
1.	$[CoCl(bsbs)(H_2O)_2]$	1605vs	1560vs	500	625	880w
2.	$[CoBr(bsbs)(H_2O)_2]$	1608vs	1562w	495	615	820w
3.	$[CoCl(bsbs)(Py)_2(H_2O)]$	1592vs	1545s	505	635	850w
4.	$[CoBr(bsbs)(Py)_2(H_2O)]$	1595vs	1543s	500	624	846w
5.*	$[CoCl(bsbs)(Py)_2]$	1590vs	1542s	515(ν_4)	655(ν_3)	870w(ν_2)
6.	$[CoCl(bsbs)(\beta\text{-pic})_2(H_2O)]$	1594vs	1542s	495	625	870br
7.	$[CoBr(bsbs)(\beta\text{-pic})_2(H_2O)]$	1596s	1548m	490	608	865w
8.	$[CoCl(bsbs)(\gamma\text{-pic})_2(H_2O)]$	1588vs	1546s	505	618	850br
9.	$[CoBr(bsbs)(\gamma\text{-pic})_2(H_2O)]$	1590s	1550s	500	600	830br
10.°	$[CoCl(bsbs)_2(\gamma\text{-pic})]$	1592s	1548m	415	675	—
11.	$[CoCl(bsbs)(Q)(H_2O)_2]$	1598vs	1552s	505	610	880br
12.	$[CoBr(bsbs)(Q)(H_2O)_2]$	1595s	1554s	500	600	820
13.	$[CoCl(bsbs)(IQ)(H_2O)_2]$	1592vs	1550s	495	630	832br
14.	$[CoBr(bsbs)(IQ)(H_2O)_2]$	1594vs	1555s	490	620	825w
15.	$[Co(NO_3)(bsbs)(H_2O)_2]$	1610s	1565w	490	645	—
16.	$[Co(bsbs)(\gamma\text{-pic})_2(H_2O)_2](ClO_4)$	1590vs	1545s	488	625	830
17.°	$[Co(bsbs)(bipy)(H_2O)_2](ClO_4)_2$	1592vs	1540s	415	705	—
18.°	$[Co(bsbs)(Phen)(H_2O)_2](ClO_4)_2$	1595vs	1565w	410	680	—

* Coordination number is 5. In all other complexes, C.N. is 6.
° Valency of Cobalt is 3. In all other complexes, valency is 2.

operated thermobalance. Analyses, molar conductance and magnetic susceptibility data are given in Table 1 and infrared and electronic spectral data are included in Table 2.

Results and Discussion

The complexes prepared now are either flaky or microcrystalline. Most of the compounds decompose before melting. They are sparingly soluble in most of the organic solvents. The low values of molar conductance Λ_m in acetone medium for all complexes excepting the perchlorate compounds indicate that they are essentially non-electrolytes. The perchlorate compounds, however are either 1 : 1 or 1 : 2 electrolytes as indicated by their Λ_m values round about 150 and 250 mhos respectively. (See Table 1). The high spin, octahedral Cobalt(II) complexes exhibit μ_{eff} values ranging between 4.8 and 5.2 B.M. indicative of the presence of 3 unpaired electrons with a large orbital contribution. Cobalt(III) ion has a d^6 configuration and usually forms diamagnetic octahedral complexes. The magnetic susceptibility values of the compounds under report clearly indicate that three of them are

Cobalt(III) complexes and in all the rest divalent cobalt is present.[8]

Infrared Spectra :

Infrared spectrum indicates the presence of the ligand bands but there is a considerable overlapping of bands due to dibenzoylmethane and the nitrogen donor ligand. The bands attributed to $\nu(C-O)$ and $\nu(C-C)$ are given in Table 2. Definite changes are observed in C–O and C–C stretching frequencies due to the introduction of the heteroligand atoms. Bands due to the heteroligand are also modified indicating their bonding to the metal ion. The bands due to $\nu(C-H)$ of dibenzoylmethane in these complexes are found to be unaffected. This rules out the possibility of the substitution reaction in the body of the ligand, in which case the composition and the analytical data would have been completely different. In the spectrum of the mixed complexes under study, broad bands are noticed (not given in the table) at $\sim 3450\ cm^{-1}$ and $\sim 1650\ cm^{-1}$ regions which can be assigned to the coordinated water molecule. A broad band arising out of $\nu(Cl-O)$ was observed in case of perchlorate complexes at $\sim 1090\ cm^{-1}$ indicating that the perchlorate groups are ionic[9] but not coordinated. The NO stretching frequency of the nitrato group observed at 1520-1480 and 1305 to 1280 cm^{-1} confirms that the coordinated nitrato group is bidentate[10].

Far-infrared Spectra :

Halogen and the nitrogen base have a tendency to form bridges resulting in polymeric forms. In general bridging M–X stretching frequencies are lower than terminal M–X stretching frequencies. In the complexes under report Cobalt-halogen and Cobalt-nitrogen stretching frequencies are observed at ~ 250 and $\sim 220\ cm^{-1}$ respectively indicating that the compounds are monomers[11-13].

Electronic Spectra :

Cobalt(II) complexes in the octahedral environment should have three spin allowed d–d transitions[14]. The bands at ~500, ~600 and at ~850 nm can be assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^2E_g$ (ν_1) transitions respectively. The electronic absorption spectrum of hexa-coordinated Cobalt(II) complexes under report is consistent with the octahedral structure[15]. The spectrum of only high-spin penta-coordinated Cobalt(II) differs considerably from other hexa-coordinated complexes of Cobalt(II) and shows three bands at 515 (ν_4), 655 (ν_3) and 870 nm (ν_2) showing its resemblance with the known[16,17] penta-coordinated species. The ν_1 absorption band could not be recorded since it is beyond the range of the instrument used. Octahedral complexes of Cobalt(III) show two principal absorption bands at ~415 and ~700 nm assignable to ${}^1A_{1g} \rightarrow {}^1B_{2g}$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$ respectively[18], indicating a distorted octahedral geometry around the metal ion.

Thermogravimetric Analysis :

Thermal decomposition of all the complexes reveals no weight loss at 105° indicating that the water molecules are not in the lattice. It was observed that the compounds of trivalent cobalt directly melt at 200° without decomposition. The pyridine and other similar adducts are observed to decompose according to the following general reactions :—

1. Co×(bzbz)$(H_2O)_2$(s) Yellow $\xrightarrow{T_1(120\text{-}150°)}$ Co×(bzbz)$(H_2O)_2$(s) Yellowish green $\downarrow T_2 < 220°$ melts

2. Co×(bzbz)$L_2(H_2O)$(s) Red micro-crystalline $\xrightarrow{T_1(110\text{-}130°)}$ Co×(bzbz)L(H_2O)(s)+L(g) Bluish black or Greenish black $\xrightarrow{T_2(130\text{-}150°)}$ Co×(bzbz)(H_2O)(s)+L(g) Blue or green $\downarrow T_3 < 200$ melts

3. Co×(bzbz)L_2(s) Orange red microcrystalline $\xrightarrow{T_1(110\text{-}130°)}$ Co×(bzbz)$(L_{3/2}$(s)+½L(g) Greenish red $\downarrow T_2 < 150$ Co×(bzbz)L(s)+½L(g) Green $\downarrow$ 165° melts

4. Co×(bzbz)L'$(H_2O)_2$(s) Yellow $\xrightarrow{T_1 < 150°}$ Co×(bzbz)L'(s) Grass green $\downarrow T_2(170\text{-}225°)$ melts

Acknowledgement

Thanks are due to U.G.C., New-Delhi for award of a teacher fellowship and to Government of Orissa Education Department for grant of leave to one of the authors (S.C.M.).

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1147-1152

Studies on Some Beryllium Complexes of Aromatic Schiff Bases†

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Manuscript received 19 September 1978, revised 9 February 1980, accepted 31 March 1980

Bis(N-salicylaldiminato)beryllium(II), bis(salicylaldoximinato) beryllium(II), bis(N-o-hydroxyphenylsalicylaldiminato)beryllium(II), mono(N-o-carboxyphenylsalicylaldiminato)beryllium(II)dihydrate and bis(N-p-aryl salicylaldiminato)beryllium(II) (where p-aryl = p-tolyl, p-anisyl, p-chlorophenyl and p-nitrophenyl) are isolated and characterised by their elemental analysis, ir and pmr spectral studies. The ir spectra of the ligands show a broad, weak to medium intensity band around 2700 cm^{-1} attributable to intramolecularly bonded OH. The ir spectra of bis(N-salicylaldiminato)beryllium(II), bis(N-salicylaldoximinato)beryllium(II) and bis(N-o-hydroxyphenylsalicylaldiminato)beryllium(II) show the presence of intermolecularly bonded NH and OH groups. Such findings are further substantiated by the pmr and mass spectral studies.

SCHIFF bases derived from the reaction of salicylaldehyde with primary aromatic amines represent a versatile series of ligands and the metal chelates of these ligands have attracted much attention[1-3]. The live interest in the Schiff bases and their metal chelates is undoubtedly due to the structural diversity of the complexes, the impracticability of applying normal coordinate methods to the assignment problem and the complexity of the spectra resulting from the presence of phenyl vibrations.

Even though quite a few papers are concerned with the studies on bidentate, tridentate and tetradentate N-alkyl or N-aryl salicylaldimines and their metal chelates with transition and non-transition metals[4-22], very meagre work on beryllium complexes of such ligands has been reported. The limited number of beryllium complexes of Schiff bases studied so far are mostly derived from N-alkyl salicylaldimine and N,N'-ethylene *bis*(salicylaldimine)[23-26] or similar Schiff bases using long chain alkyl amines.

The work presented here deals with the syntheses of some new beryllium complexes of bidentate and tridentate N-aryl salicylaldimines and the ir and pmr spectral studies of these complexes.

Experimental

Materials and Methods :

Salicylaldehyde (Sarabhai Merck, LR grade) was distilled under reduced pressure. Aniline derivatives were purified by recrystallisation from alcohol. Aniline, *p*-toludine, *p*-anisidine, *p*-chloroaniline, *p*-nitroaniline, *o*-aminophenol and anthranilic acid were of C.P. grade. Salicylaldoxime and beryllium nitrate, $Be(NO_3)_2 3H_2O$, were of AR grade. The beryllium content was determined by standard method[27].

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Model 221. The pmr spectra were recorded on a Varian Associate, Model T-60 spectrometer operating at 60 Mc/s with TMS as an internal standard. The mass spectra were recorded on CEC 21-110B (USA) double focussing mass spectrometer at a voltage of 70 eV.

Preparation of ligands and their beryllium chelates :

N-aryl salicylaldimines were prepared according to reported methods[7,11,28,29]. Although N-salicylaldimine could not be isolated in solid state by the reported method[11], its beryllium chelate could be prepared by reacting *bis*(salicylaldehydato)beryllium(II) with ammonia *in situ*. All other beryllium chelates reported here were prepared by the following procedure :

N-*p*-tolylsalicylaldimine (0.02 moles) was dissolved in methanol or ethanol (50 ml) and to the clear solution, an aqueous alcoholic beryllium nitrate solution (0.01 mole) in 10 ml was added. The resulting clear yellow solution was refluxed for about an hour on water bath, the *p*H of the solution was adjusted to ~7 with dilute ammonia (1 : 1) and it was further refluxed. The precipitated yellow solid was filtered on cooling, washed with cold alcohol till free of unreacted ligand, and air or vacuum dried. Mono(N-*o*-carboxyphenyl-salicylaldiminato)-beryllium(II) dihydrate was prepared in a similar manner.

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TABLE 1—ELEMENTAL ANALYSES OF N-ARYL SALICYLALDIMINES AND THEIR BERYLLIUM CHELATES

No.	Name	m.p. °C	C	H	N	Be%
1.	N-phenylsalicylaldimine $C_{13}H_{11}NO$	51	79.15 (78.68)	5.62 (5.78)	7.10 (7.24)	— —
2.	*Bis*(N-phenylsalicylaldiminato)-beryllium(II) $Be(C_{13}H_{10}NO)_2$	—	78.17 (77.81)	5.58 (4.99)	7.19 (6.98)	2.18 (2.25)
3.	N-*p*-tolylsalicylaldimine $C_{14}H_{13}NO$	97	78.96 (79.22)	6.88 (6.65)	6.19 (6.60)	— —
4.	*Bis*(N-*p*-tolylsalicylaldiminato)-beryllium(II) $Be(C_{14}H_{12}NO)_2$	242	79.56 (77.98)	6.02 (6.07)	6.57 (6.49)	2.18 (2.09)
5.	N-*p*-anisylsalicylaldimine $C_{14}H_{13}NO_2$	89	78.63 (73.66)	6.02 (6.18)	6.28 (6.14)	— —
6.	*Bis*(N-*p*-anisylsalicylaldiminato)-beryllium(II) $Be(C_{14}H_{12}NO_2)_2$	118	73.77 (72.81)	5.60 (5.21)	5.92 (6.07)	2.03 (1.95)
7.	N-*p*-chlorophenyl-salicylaldimine $C_{13}H_{10}NOCl$	110	67.19 (67.39)	4.67 (4.35)	6.00 (6.05)	— —
8.	*Bis*(N-*p*-chlorophenylsalicylaldiminato)-Beryllium(II) $Be(C_{13}H_9NOCl)_2$	260	66.97 (66.38)	4.11 (3.86)	5.98 (5.96)	1.88 (1.92)
9.	N-*p*-nitrophenylsalicylaldimine $C_{13}H_{10}N_2O_3$	163-64	64.42 (64.46)	4.41 (4.16)	11.03 (11.57)	— —
10.	*Bis*(N-*p*-nitrophenylsalicylaldiminato) beryllium(II) $Be(C_{13}H_9N_2O_3)_2$	320	62.69 (63.54)	4.61 (3.69)	12.52 (11.40)	1.68 (1.83)
11.	N-*o*-hydroxyphenylsalicylaldimine $C_{13}H_{11}NO_2$	194	72.17 (73.22)	5.40 (5.20)	6.58 (6.57)	— —
12.	*Bis*(N-*o*-hydroxyphenylsalicylaldiminato) beryllium(II) $Be(C_{13}H_{10}NO_2)_2$	203-5	71.50 (72.06)	4.80 (4.62)	6.72 (6.47)	2.01 (2.03)
13.	N-*o*-carboxyphenylsalicylaldimine $C_{14}H_{11}NO_3$	212	69.21 (69.70)	4.50 (4.60)	5.97 (5.81)	— —
14.	Mono(N-*o*-carboxyphenylsalicylaldiminato) beryllium(II)dihydrate $Be(C_{14}H_9NO_3)2H_2O$	>350	60.15 (59.15)	5.12 (4.58)	4.55 (4.93)	3.13 (3.17)
15.	*Bis*(salicylaldoximinato) beryllium(II) $Be(C_7H_6NO_2)_2$	298	60.31 (59.78)	4.98 (4.27)	10.50 (9.96)	3.15 (3.21)
16.	*Bis*(N-salicylaldiminato)-beryllium(II) $Be(C_7H_6NO)_2$	250	66.76 (67.46)	5.03 (4.82)	10.78 (11.25)	3.58 (3.62)

Calculated values are given in the parenthesis.

Beryllium chelates of N-phenyl, N-*p*-anisyl, N-*o*-hydroxyphenyl-salicylaldimine and salicylaldoxime were prepared by a modified method. Instead of using preformed ligands, the starting reactants were mixed in required amounts in alcohol using freshly prepared beryllium hydroxide and the mixture was refluxed on water bath till all the hydroxide disappeared. The solution was concentrated and cooled and the solid obtained was filtered, washed free of unreacted ligands with small volumes of cold alcohol and air or vacuum dried.

In the preparation of beryllium chelates of N-*p*-chlorophenylsalicylaldimine and N-*p*-nitrophenylsalicylaldimine, the preformed ligand (0.02 mole) was dissolved in a few ml of acetic acid (2-5 ml) and then diluted with aqueous alcohol. The clear solution of the ligand was then reacted with an aqueous solution of beryllium nitrate (0.01 mole, in 10-15 ml H_2O). The *p*H of the clear solution was adjusted to ~7 with dilute ammonia solution (1 : 1) and the resulting voluminous precipitate was digested on water bath for about 1 hour. The crystalline, yellow precipitate was filtered while hot, washed with alcohol till free of unreacted ligand and air or vacuum dried.

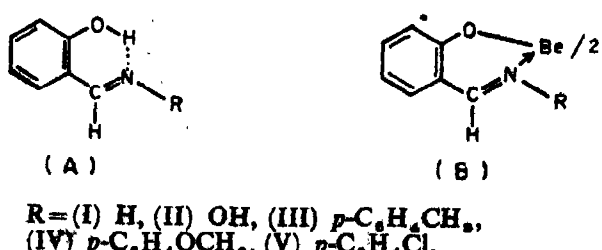
Most of the beryllium chelates were insoluble or sparingly soluble in common organic solvents. The elemental analyses, m.p. are given in Table 1.

Results and Discussion

Although three and two coordinated beryllium compounds are known under special conditions, beryllium prefers usually four coordination[80].

The Schiff bases studied here are found to form tetrahedral 1 : 2 metal-ligand complexes with beryllium. These compounds are yellow in colour and have high melting points, a few of them melt with decomposition. The solubility of these complexes in common organic solvents is quite low as expected, but most of them dissolve in DMSO to an appreciable extent which was used to study their pmr spectra.

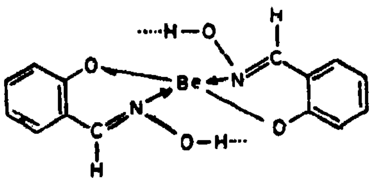
The probable structure of the beryllium chelates and the ligand are given below :



(A) (B)

R=(I) H, (II) OH, (III) *p*-$C_6H_4CH_3$, (IV) *p*-$C_6H_4OCH_3$, (V) *p*-C_6H_4Cl, (VI) *p*-$C_6H_4NO_2$, (VII) *o*-C_6H_4OH (VIII) *o*-C_6H_4COOH.

In the ligands an intramolecular hydrogen bond is formed resulting in a stable six-membered ring, since no absorption bands due to free O – H stretching vibration are found in the expected region; instead a broad and weak band is found in the region around 2700 cm^{-1} as reported by Baker and Shulgin[31] and others[32,33]. This band disappears in the spectra of all the beryllium complexes which confirms the above assignment and indicates chelate formation. In the infrared spectrum of salicylaldoxime, two bands at 3365 cm^{-1} and 3000 cm^{-1} are assigned to the intermolecularly and intramolecularly bonded OH stretching vibrations respectively[34]. Sen and coworkers[35] have assigned the three bands found at 3600 cm^{-1}, 3445 cm^{-1} and 3230 cm^{-1} in the CCl_4 solution spectrum of the compound to free, intermolecularly and intramolecularly bonded OH stretching vibrations respectively. The spectrum of *bis*(salicylaldoximinato)-beryllium(II) shows a broad band at ~2750 cm^{-1} which is due to intermolecularly bonded OH groups as shown below:



The spectrum of N-*o*-hydroxyphenylsalicylaldimine (HCB/Nujol mull, Fig. 1) shows two broad and weak bands at 2500 cm^{-1} and 1850 cm^{-1} which may be due to a double minimum potential hydrogen bond[36] of the intramolecularly bonded

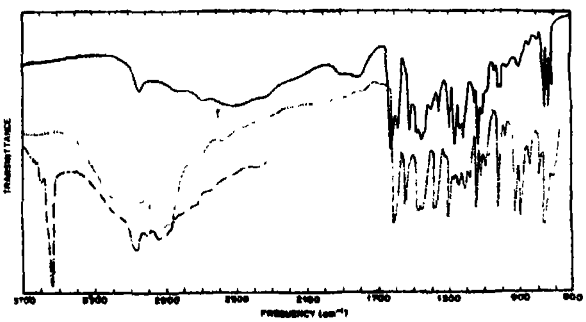


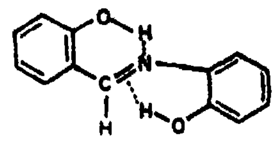
Fig. 1. Infrared Spectra of:

—N-*o*-Hydroxyphenylsalicylaldimine in HCB/Nujol Mull

...*Bis*(N-*o*-Hydroxyphenylsalicylaldiminato) Beryllium(II) in Nujol Mull

—.—.— N-*o*-Hydroxyphenylsalicylaldimine in CCl_4 Solution (0.01*M*)

phenolic OH. The band due to amine OH group is not observed separately. The CCl_4 solution spectrum of this ligand (Fig. 1) shows a strong band at 3540 cm^{-1}, associated with a weak band at 3590 cm^{-1} and a second broad, medium intensity band at around 3000 cm^{-1}. The sharp strong band at 3540 cm^{-1} may be assigned to the O – H...π interaction and the associated weak band at 3590 cm^{-1} to free OH stretching vibrations. The lower frequency band at ~3000 cm^{-1} is attributed to phenolic OH intramolecularly bonded to the nitrogen atom of the azomethine group. Such findings are reported by Baker and Shulgin[31] and they have assigned bands at 3546 cm^{-1} and 2730 cm^{-1} to O – H...π and OH...N intramolecular bonds respectively as shown in the figure for N-*o*-hydroxyphenylsalicylaldimine.



The existence of OH..π bonds have also been reported by Oki and Iwamura[37]. Very recently, Malek and Alyea[16] have studied N-*o*-hydroxyphenylsalicylaldimine in halocarbon mull and DMSO and assigned the bands in the region 3500-2900 cm^{-1} to OH stretching vibration. These authors have assigned a band near 3500 cm^{-1} to phenolic OH bonded to nitrogen and the band at ~2900 cm^{-1} to amine OH bonded to π electrons. This appears to be contradictory to Baker and Shulgin[31] and our findings. The infrared spectrum of all other N-aryl salicylaldimines containing only phenolic OH group have shown only one broad and weak band at ~2700 cm^{-1} which is due to intramolecular bonding of OH to nitrogen. It is clear from above data that the π-bonded hydrogen bond exists as weak band and appears near 3600 cm^{-1} showing a little shift from free OH region. The similarity of N-*o*-hydroxyphenylsalicylaldimine and N-salicylaldimine to salicylaldoxime led us to expect intermolecularly bonded O – H or N – H groups in the beryllium complexes of these ligands. It is interesting to observe a broad medium intensity band at 3110 cm^{-1} in the case of *bis*(N-*o*-hydroxyphenylsalicylaldiminato)beryllium(II) (Fig. 1) and two medium bands in *bis*(salicylaldiminato)beryllium(II) attributed to intermolecularly bonded OH and N – H groups respectively.

Assignment of characteristic νC=N, νC=C bands in the region of 1700-1500 cm^{-1} is difficult due to extensive vibrational coupling and the complexity of the spectra resulting from the presence of phenyl vibrations and the two different metal-ligand bonds (M – O and M – N). In a non-conjugated system C = N normally appears in the 1690-1650 cm^{-1} region; conjugation shifts it to lower frequency and it is usually found at ~1630 cm^{-1} for the Schiff bases[18]. However, the reported ir spectra are generally restricted to the assignments of C=N, C=C and C – O bands[12,13]. Very recently ir study on ^{15}N-labelling has been reported[19,38], on the aryl Schiff bases in order to ascertain the C=N,

C=C and C–O bands in these ligands and their metal chelates. Percy and Thornton[43] have found two ^{15}N-sensitive bands near 1600 cm^{-1} and 1570 cm^{-1} to occur in the spectra of N-aryl salicylaldimines. It was the higher frequency band that has been emperically assigned so far[13] to the νC=N. The lower frequency band that exhibits a greater ^{15}N-induced shift is found to be more vibrationally pure. Considering the above facts, these workers have assigned bands at 1627 cm^{-1} and 1579 cm^{-1} in N-*p*-anisylsalicylaldimine, 1625 cm^{-1} and 1579 cm^{-1} in N-phenylsalicylaldimine and 1613 cm^{-1} and 1573 cm^{-1} band in N-*p* chlorophenylsalicylaldimine to C=N frequency. Further, it was observed that the band at ~1600 cm^{-1} shifts a little to lower frequency but the band at 1570 cm^{-1} shows considerable lowering (20-30 cm^{-1}) on complex formation. In the beryllium complexes, we have found that these bands show shifts as reported and therefore can be assigned to C=N stretching vibration.

The 1600 cm^{-1} νC=N band occurs at higher frequency when electron donating groups such as CH_3, OCH_3, OH are attached to ortho or para position in the aniline ring and at lower frequency when electron withdrawing groups such as chloro or nitro are attached at para position in the aniline ring. The second νC=N band is found between 1570-1565 in all these ligands except in N-*o*-hydroxyphenylsalicylaldimine and salicylaldoxime where it occurs at 1585 cm^{-1} and 1570 cm^{-1} respectively[34]. The bands appearing in the region of 1500-1300 cm^{-1} in the ligands as well as in beryllium chelates are due to aromatic CH and =CH vibrations[10]. The characteristic strong band at 1280 cm^{-1} which is present in all the aromatic salicylaldimines is assigned to phenolic νC–O+δOH stretching vibrations[10]. This band on complex formation with beryllium disappears and a new band is found in the region of 1300-1325 cm^{-1} which is due to bonded phenolic νC–O vibration. Another strong band at 1185-1190 cm^{-1} present in ligands as well as beryllium chelates may be assigned to aryl carbon-nitrogen stretching vibrations[30]. This band does not show any change even when a substituent is introduced in the *p*-position of aniline ring. The strong band at 1140 cm^{-1} present both in the ligands and their metal chelates may be assigned to azomethine C–H stretching vibration[10].

The spectra in the region 1100 cm^{-1} and below are much more complicated due to the presence of phenyl ring, M–O and M–N vibrations. However, the band at 930-945 cm^{-1} in beryllium chelate is due to metal-ligand stretching[46,47] and bands in the region 800-750 are due to aromatic CH vibrations[40].

In order to get clearer insight of these ligands and their beryllium chelates, the pmr spectral study has been carried out.

The strong intramolecular hydrogen bonding present in the ligands leads to a very broad and weak hydroxyl absorption near 2700 cm^{-1} so that the pmr spectra are more informative than ir spectra with respect to the nature of O–H bonding. It has been shown that N-aryl salicylaldimines exist solely in the phenolimine form in non-hydroxylic solvents at normal temperatures[14,41,42]. Any significant presence of the keto-amine form would split the signal arising from the azomethine proton. No splitting of this signal is observed in the pmr spectra of ligands studied here, nor the aromatic proton signals displaced from its normal position. From these data it is assumed that N-aryl salicylaldimines possess the phenolimine structure. The bonded O–H proton signals are found between 12.1δ to 13.85δ for N-aryl salicylaldimines and at 8.18δ and 9.95δ for salicylaldoxime[48]. This assignment has been verified by deuterium exchange. In ligands, the sharp singlet of azomethine proton is found between 8.18δ to 9.2δ. The signals due to $-CH_3$ protons in N-*p*-tolyl and N-*p*-anisylsalicylaldimines and their beryllium chelates are found at 2.34δ, 2.53δ, 3.80δ and 3.93δ respectively. The ring protons of aldehyde and aniline appear in the region between 6.5δ-8.33δ. In the pmr spectrum of N-*o*-hydroxyphenylsalicylaldimine two signals are found at 13.35δ and 8.30δ. The signal at 8.30δ is assigned to *o*-hydroxy proton of aniline, whereas the 13.35δ signal is assigned to hydrogen bonded aldehyde O–H proton, both disappear on deuteration. In the pmr spectra of all the beryllium chelates, the signal at 12δ to 13.85δ due to phenolic OH proton is absent indicating the participation of the O–H in chelate formation. The signals due to ring protons, azomethine proton and others show no change in their position, but in case of beryllium chelate of N-*o*-hydroxyphenylsalicylaldimine two signals for azomethine CH-proton are found at 8.40δ and 9.03δ. In the pmr spectrum of *bis*-(N-*o*-hydroxyphenylsalicylaldimine) beryllium(II) (recorded in DMSO), two broad signals at 13.85δ and 9.70δ were found. This is presumably due to presence of hydrogen bonded protons as found in salicylaldoxime complexes.

In the spectrum of *bis*(salicylaldiminato) beryllium(II) (Fig. 2) a doublet is found at 9.97 δ (J=13 Hz) due to N–H protons. This is confirmed by the disappearance of these signals on deuteration. Furthermore, the presence of the doublet also indicates that the two N-H protons are coupled with CH proton of azomethine group. The signal due to CH proton also appears as a doublet at 8.47 δ (J=13 Hz) which is due to coupling between CH and N-H protons. This doublet collapses into a singlet on deuteration.

The beryllium complex of salicylaldoxime also shows two signals at 10.13 δ and 11.30 δ, both disappearing on deuteration. These signals may be due to hydrogen bonded OH. The above data supports

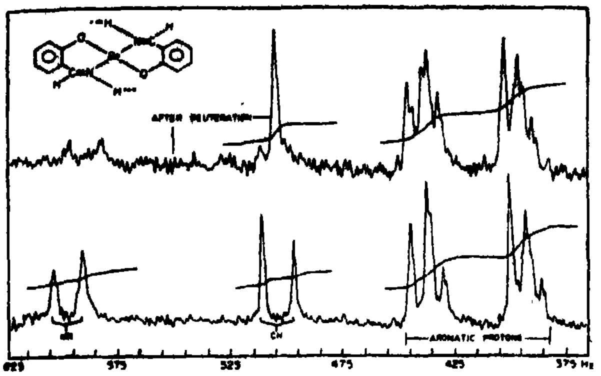
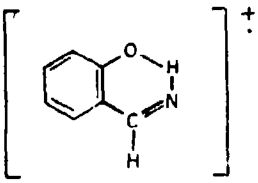


Fig. 2. PMR Spectrum of *Bis*(N-Salicylaldiminato)beryllium(II) in Dry DMSO.

the conclusion drawn from the ir studies on these ligands and their beryllium chelates.

The mass spectra of the ligands show base peak at m/e 197, 211, 227, 231, 241, 212, 241 for N-phenyl, N-*p*-tolyl, N-*p*-anisyl, N-*p*-chlorophenyl, N-*p*-nitrophenyl, N-*o*-hydroxyphenyl and N-*o*-carboxyphenylsalicylaldimines which are also the molecular ion peaks. The high intensity of the molecular ion peaks is in accordance with the stabilization of the molecule by strong intramolecular hydrogen bonding. Similarly the high resistance of the ligand to hydrolysis reflects the stabilization of the azomethine bond by means of the hydrogen bonded ring system. Furthermore, it is noteworthy that a strong peak at m/e 120 can be assigned to the fragment shown below. This usually occurs with hydrogen transfer resulting in a cluster of peaks at m/e 121, 120, 119. The formation of such stable



m/e 120

heterocyclic species is characteristic of the mass spectra of ortho substituted aromatic Schiff bases[44,45]. The spectra of N-*p*-tolyl, N-*p*-anisyl, N-*p*-chloro ligands show loss of the *p*-substituted groups resulting in metastable ions. Similarly, the spectra of N-*o*-hydroxyphenyl and N-*o*-carboxyphenylsalicylidimines show loss of water and carbon dioxide from molecular ion. Another characteristic feature of these Schiff bases is the formation of a species of m/e 168-169. The formation of such a fragment may be due to the loss of CO and the *p*-substituent with proton transfer.

Apart from these major peaks, these spectra also show a peak at m/e 77 corresponding to $C_6H_5^+$ ion formed by the breakdown of the parent ion. These spectra show that fission at the ring nitrogen bond is more facile than at the ring carbon-bond. The mass spectra of para substituted Schiff bases show essentially the same features, sometimes complicated by the effect of substituents.

It is concluded from the above studies that beryllium forms strong bonds with oxygen and nitrogen containing ligands. It was found that the beryllium complex has the same stability as copper complexes which contradicts the apparent belief that beryllium bonds weakly with ligands containing nitrogen donor atoms[46]. It is also found that N-aryl salicylaldimine beryllium complexes are as stable as the N-alkyl salicylaldimine complexes. The tridentate dibasic ligand, N-*o*-hydroxyphenylsalicylaldimine acts as a monobasic, bidentate ligand towards beryllium, where the amino –OH group takes part only in hydrogen bonding as is found in case of salicylaldoxime. It is interesting to note that N-*o*-carboxyphenylsalicylaldimine acts as a dibasic ligand with beryllium.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1153-1155

Solid State Studies of Sodium and Potassium Salts of Mixed Heteropoly Molybdotungstoselenite and Molybdotungstotellurite

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Manuscript received 15 April 1980, revised 7 August 1980, accepted 9 September 1980

The possibilities of using a solid phase reaction between $Na_2WO_4-H_2SeO_3-H_2MoO_4$ and $Na_2WO_4-H_2TeO_3-H_2MoO_4$ have been studied to establish the methods of synthesis of mixed heteropoly complexes $Na_6[WSeMo_8O_{32}]18H_2O$ and $Na_6[WTeMo_8O_{32}]20H_2O$ respectively. Their potassium salts have also been prepared. Preliminary X-ray diffraction studies showed the molecular weights of the compounds to be 1980 and 2054 with space groupings D_{2h}^1-P_{nnn} and $I4_1/a$ respectively. The molecular weights of the potassium salts of the compounds as shown by X-ray studies are 2002 and 2262 respectively. The thermal decomposition analysis of the compounds have also been carried out.

THE W-Se-Mo-O and W-Te-Mo-O systems are of much interest due to their application in the oxidation of olefines to unsaturated carboxylic acids[1]. So far, however, there has been no systematic investigations of solid state studies of these systems. The properties of cobalt salts of molybdoselenates and molybdotellurates, by a solid state reaction[2] have been recently reported[3] but they are of very little interest with the present communication. In these systems the position of selenium and tellurium is of much importance because they are active in the oxidation of propylene to acrylic acid[4]. Solution phase studies of W-Te-V system have though been carried out by Nikitina *et.al*[5] and Derkach *et.al*[6], no evidences of studies of W-Se-Mo and W-Te-Mo systems are found in chemical literature either in solid or in solution phase.

Experimental

Synthesis of Sodium-9-Heteropoly Molybdotungstoselenite $Na_6[WSeMo_8O_{32}]$ $18H_2O$. (I) :

1.29 gm of selenious acid (H_2SeO_3), 10.15 gm of molybdic acid ($H_2MoO_4.H_2O$) and 3.3 gm of sodium tungstate ($Na_2WO_4.2H_2O$), all of B.D.H. make, were taken in a platinum crucible, mixed thoroughly and heated for 8 hrs at 850° in a muffle furnace. The fused mass was digested with 50 ml of water (*p*H 3.2), evaporated to half of its original volume and left for a few days. Long needle-shaped white transparent crystals, slowly separated out and were collected after 6 days. The compound was recrystallized from hot water mixed with a few drops of alcohol.

Synthesis of Sodium-9-Heteropoly Molybdotungstotellurite $Na_6[WTeMo_8O_{32}]$ $20H_2O$. (II) :

For the synthesis of this complex, 1.78 gm of tellurous acid (H_2TeO_3), 10.15 gm of $H_2MoO_4.H_2O$ and 3.3 gm of $Na_2WO_4.2H_2O$ were taken in a platinum crucible and mixed thoroughly. The charge was heated for 8 hrs at a controlled temperature of 950° in a muffle furnace. The fused mass was digested with 50 ml of water (*p*H 2.4). The *p*H of the aqueous solution was raised to 4.5 by adding 25 ml of a warm solution of 5% aqueous sodium tungstate. The solution was reduced to two-third of its original volume by heating it on a water bath and left for crystallization. Small white shining crystals were collected after an interval of 4 days. The compound was recrystallized thrice from hot water. To get a single isolated crystal of the compound for X-ray studies, here, the *p*H was raised a little higher (4.5) because white curdy compound would have found to be separated from the aqueous solution (*p*H 2.4) as such.

The potassium salt of compound (I) was prepared by adding 100 ml of $K_2S_2O_8$ solution (0.51 gm of $K_2S_2O_8$ dissolved in 100 ml of water) in small portions to an aqueous boiling solution of compound I (2 gm of compound I dissolved in 100 ml of water). Similarly the potassium salt of compound(II) was prepared by adding 100 ml of $K_2S_2O_8$ solution (0·47 gm of $K_2S_2O_8$ dissolved in 100 ml of water) in small portions to an aqueous boiling solution of compound II (2.09 gm of compound II, dissolved in 100 ml of water). Pale yellow and cream coloured crystals were separated on cooling from compounds(I) and (II) respectively.

Methods of Analysis :

For analysis, the complexes were completely broken by boiling with hot water along with a few pellets of NaOH and neutralizing by dil. H_2SO_4.

The total content of molybdenum and tungsten in the compounds were determined by using two methods :

Molybdenum was determined : (i) Colorimetrically, using ammonium thiocyanate[7] and measuring absorption at 520 mμ and (ii) Gravimetrically in the form of lead molybdate[8].

Tungsten content was determined : (i) Colorimetrically, using hydroquinone[7] and measuring the absorption at 570 mμ and (ii) Gravimetrically, using α-benzoin-oxime[8].

The interference of Mo(VI) during the estimation of W(VI) was removed by precipitating them simultaneously by α-benzoinoxime. The precipitate was heated to 525°, cooled and dissolved in 1 : 3 ammonia solution whereby tungsten passed into solution leaving behind molybdenum in the precipitate. From the filtrate, tungsten was estimated as WO_3 by cinchonine hydrochloride method[8].

Selenium content was determined : (i) Colorimetrically using potassium iodide[7] and (ii) Gravimetrically, using hydrochloric acid solution[8] for the separation of elementary selenium.

Tellurium content was determined : (i) Colorimetrically, using potassium iodide[7] and (ii) Gravimetrically using hydrochloric acid solution[8] for the separation of elementary tellurium.

Sodium and potassium contents were found out by flame photometer.

Hydrogen was estimated by element estimation technique.

From the analytical data the compounds were formulated : (Found Mo, 38.28 ; W, 9.11 ; Se, 3.92 ; Na, 6.83 ; H, 1.83 ; calc. for $Na_6[WSeMo_8O_{32}]$ $18H_2O$: Mo, 38.30 ; W, 9.18 ; Se, 3.99 ; Na, 6.88 ; H, 1.84%).

(Found Mo, 36.70 ; W, 8.78 ; Te, 6.11 ; Na, 6.59 ; H, 1.90 ; calc. for $Na_6[WTeMo_8O_{32}]$ $20H_2O$; Mo, 36.75 ; W, 8.80 ; Te, 6.12 ; Na, 6.60 ; H, 1.91%).

(Found Mo, 37.80 ; W, 9.0 ; Se, 3.42 ; K, 11.00 ; H, 1.36 ; calc. for $K_6[WSeMo_8O_{32}]$ $14H_2O$: Mo, 37.85 ; W, 9.07 ; Se, 3.88 ; K, 11.53 ; H, 1.38%).

(Found Mo, 33.89 ; W, 7.99 ; Te, 5.52 ; K, 10.20 ; H, 2.25 ; calc. for $K_6[WTeMo_8O_{32}]$ $26H_2O$: Mo, 33.47 ; W, 8.02 ; Te, 5.58 ; K, 10.20 ; H, 2.27%).

The final representation of the formulae of the compounds were according to the view suggested by Pauling *et al*[9]. for the parent heteropoly anion $[X^nMo_9O_{32}]^{-(10-n)}$.

X-ray Diffraction Studies of the Compounds :

X-ray crystal diffraction analyses of compound (I) and (II) showed that they are isostructural. Photographs of a single crystal of sodium-9-molybdotungstoselenite reveal for $Na_6[SeMo_8WO_{32}]$ $18H_2O$ a orthorhombic cell, a = 12.56, b = 15.15, c = 9.85 Å and $\alpha=\beta=\gamma=90°$, volume per unit cell, V = 1876 Å^3. The space group is D^2_{2h}-P_{nnn}. The number of unit cell contained Z = 2. measured density, Dm = 3.5 gcc^{-1}. The molecular weight, $M_{obs.}$ of the compound, calculated from the relation $Dm = \frac{1.66\ M.Z}{V}$ comes to 1980 as compared with the calculated value 2004. The results of the X-ray crystal diffraction studies for the other compounds are given below :

(II) $K_6[SeMo_8WO_{32}]$ $14H_2O$: a = 14.21, b = 9.24, c = 14.50 Å, $\alpha=\beta=\gamma=90°$, V = 1903.76 Å^3, Orthorhombic system, Z = 2, Dm = 3.4 gcc^{-1}, $M_{obs.}$ = 2002 against M calc = 2029.

(III) $Na_6[TeMo_8WO_{32}]$ $20H_2O$: a = 17.23, b = 10.56, c = 12.12 Å, $\alpha=\beta=\gamma=90°$, V = 2205.21 Å^3, Z = 2, space group I 4 1/a, Dm = 3.0 gcc^{-1}, $M_{obs.}$ = 2054 against M calc. = 2089.

(IV) $K_6[TeMo_8WO_{32}]$ $26H_2O$: a = 16.79, b = 10.21, c = 15.30 Å, $\alpha=\beta=\gamma=90°$, Orthorhombic system, V = 2622.74 Å^3, Z = 2, Dm = 2.7 gcc^{-1}, M_{obs} = 2262 against M calc = 2293.

Thermal Behaviour of the Compounds :

The heteropoly acids and their salts can be regarded as condensation inorganic polymers[10]. To know stepwise loss of water molecules and the final decomposition temperature of the compound, their thermal degradation studies[10] have been made at different temperatures on the basis of the investigations made by West and Audrith[11] on a few heteropoly compounds. Known amounts of the samples were taken in a platinum crucible, heated in a controlled high temperature furnace and the samples were weighed and analysed successively at different temperatures. The systematic loss of water molecules and the surrounding optimum temperature at which the compounds were broken as a whole into

its lower oxides are tabulated below :

Compounds	Loss of water molecules						*Decomposition Temp. °C
	60°	120°	200°	300°	400°	500°	
(1) $Na_6[WSeMo_8O_{32}]18H_2O$	—	2 mol	1 mol	4 mol	4 mol	—	750±10
(2) $Na_6[WTeMo_8O_{32}]20H_2O$	—	3 mol	2 mol	5 mol	2 mol	—	820±10
(3) $K_6[WSeMo_8O_{32}]14H_2O$	—	3 mol	1 mol	4 mol	—	—	725±10
(4) $K_6[WTeMo_8O_{32}]26H_2O$	—	2 mol	1 mol	7 mol	5 mol	2 mol	780±10

* Decomposition of the compounds into their lower oxides.

From the above table it is clear that in all the heteropoly salts prepared, their water of crystallization eliminated out nearly in 400-500° range. Rest 6 to 8 water molecules remained intact in the crystal lattice as the water of constitution. The number of water of constitution in the compounds agreed closely with the views of Scroggie and Clark[12] with comparable compounds. To remove water of constitution, the compounds were heated to a still higher temperature. Nearly at 750 to 820±10° the compounds were broken as a whole into the basic units of lower oxides of the constituent metals.

Discussion

The representative mixed heteropoly compounds prepared here are basically 1 : 9 heteropoly molybdates of the present heteroanion $[X^nMo_9O_{32}]^{-(10-n)}$ where one MoO_6 octahedra has been replaced by one WO_6 octahedron. The structures of these heteropoly compounds will be similar to that of Pauling's[9] heteroanion $[X^nMo_9O_{32}]^{-(10-n)}$ with a slight distortion due to the replacement of one of MoO_6 octahedra by one WO_6 octahedron. Comparing the thermal stabilities of the compounds with those of silicomolybdates[12] and phosphomolybdates[13] it may be concluded that greater the positive charge on the central ion $[Mo_9O_{32}]^{-10}$, more effective is the binding in the resulting heteropoly anion, stablizing the latter against thermal vibrations and resultant decomposition.

Acknowledgement

The authors wish to record their sincere thanks to the authorities of C.M.R.I.E., Durgapur and F.R.I., Dhanbad for their active co-operation in X-ray work. The authors are also thankful to Prof. H. C. Mishra, Head of the Department of Chemistry, Ranchi University for facilities.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1156-1158

Amperometric Determination of Ag(I), Au(III), Hg(II) and Pd(II) with Thiosalicylamide

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Manuscript received 31 July 1978, revised 6 November 1979, accepted 9 September 1980

A rapid method for the amperometric determination of Ag(I), Au(III), Hg(II) and Pd(II) with thiosalicylamide at the rotating platinum electrode has been developed. Thus, 0.409 to 3.191 mg Ag(0.252-1.960 mM), 0.085 to 4.275 mg Au(0.0216-1.080 mM), 0.420 to 6.970 mg Hg(0.131-2.170 mM) and 0.071 to 1.860 mg Pd(0.0475-1.240 mM) are amperometrically determined in acid medium using thiosalicylamide as a complexing agent. All the four metals are determined in presence of large number of diverse ions, e.g., Cd(II), Zn(II), Pb(II), Mn(II), Ni(II), Co(II), Cr(III), Fe(III), Al(III), As(III), Sb(III), Bi(III), V(V), Zr(IV), etc. The relative mean errors in the determination of Ag, Au, Hg and Pd are found to be 0.078%, 0.935%, 1.362% and 0.434% respectively. The voltammetry of thiosalicylamide at a rotating platinum electrode is also investigated.

A survey of the existing literature reveals the applications of thiosalicylamide[1] (*o*-hydroxy thiobenzamide) as a successful gravimetric and spectrophotometric reagent. Recently, thiosalicylamide has been found to be suitable as a sulphide precipitating amperometric reagent[2] in this laboratory. Unlike thioacetamide[3], which is susceptible to easy oxidation to its disulphide, thiosalicylamide solution is quite stable both in aqueous and alcoholic medium. Probably, the intramolecular H-bond from the ortho OH inhibits the process of easy oxidation of thiosalicylamide.

In the present investigation, thiosalicylamide has been used in the amperometric determination of Ag(I), Au(III), Hg(II) and Pd(II) at the rotating platinum electrode. In acid medium, the metals form water insoluble complexes with thiosalicylamide. From the titration results, the mole ratio of metal-ligand in the complexes of Ag(I), Au(III), Hg(II) and Pd(II) were determined and found to be 1 : 1, 1 : 3, 1 : 2, and 1 : 4 respectively, which corroborated the earlier results observed in this laboratory[1]. Silver and mercury complexes of thiosalicylamide are white in colour, while those of gold and palladium are orange yellow and yellow respectively. Compared to earlier investigations[4-7] for the amperometric determinations of Ag(I), Au(III), Hg(II) and Pd(II), the present method is sufficiently sensitive and effective, particularly in presence of large number of diverse ions.

In the voltammetry of thiosalicylamide, the variation of the anodic current with respect to the potential applied on the rotating platinum electrode at different acidities has been investigated.

* Senior Author.

Experimental

Reagent and Chemicals :

Thiosalicylamide was prepared and purified[8]. One hundred millilitre standard thiosalicylamide solution (0.05*M*) was prepared in 20% ethanol and the weaker solutions were made with proper dilution. The strength of thiosalicylamide solution was checked by iodimetry[1]. The stock solutions of $AgNO_3$, $AuCl_3$, $HgSO_4$, and $PdCl_2$ were prepared in double distilled water and the metals were estimated by the usual gravimetric methods.

Apparatus :

The voltammetry studies were carried out in Radelkis pen recording polarograph (Type OH 101/1). Amperometric titrations were performed with Toshniwal manual polarograph. Cambridge *p*H meter (Bench Model) was used for measuring *p*H.

Voltammograms of thiosalicylamide :

The voltammograms of thiosalicylamide were recorded at rotating platinum electrode in KCl (0.50 *M*) supporting electrolyte at 25°, while the *p*H were maintained by HCl and citric acid-Na_2HPO_4 buffer (Fig. 1). On applying an external potential of magnitude zero(0) to 1.10 volt (vs. S.C.E), the i-v curves of thiosalicylamide shows two waves. On increasing *p*H, both the waves were shifted towards more negative potential. The voltammograms of thiosalicylamide at different concentrations were recorded at 25° and it was found that the limiting currents were proportional to the concentrations of thiosalicylamide (1.00 mM-0.05 mM).

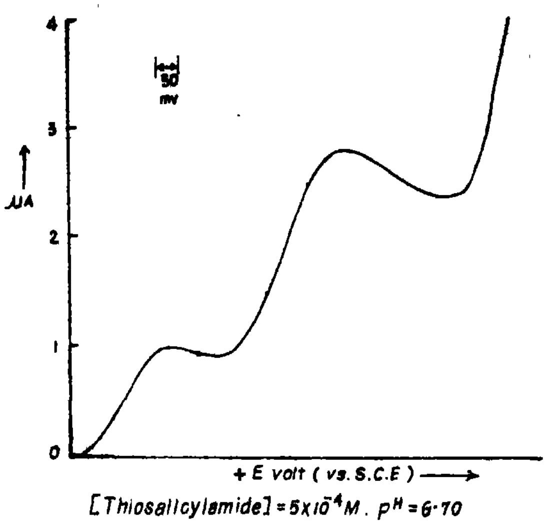


Fig. 1. Voltammogram of thiosalicylamide at R. P. E

Procedures of amperometric titrations :

An aliquot of the metal solution was taken into a three necked titration cell in which successively requisite amount of acid and supporting electrolyte were added followed by dilution to a definite volume (about 14-20 ml). The acidities of Ag(I), Au(III), Hg(II) and Pd(II) solutions were 4*N* H_2SO_4, 3*N* HCl, 0.126 *N* HCl and 4*N* HCl respectively. The cell was then placed in a thermostat, at 30°. The silver solution was deaerated by passing pure nitrogen, while no such deaeration was required in the cases of Au, Hg and Pd. Meanwhile, the rotating platinum electrode and the saturated calomel electrode were introduced inside the solution through the necks of the cell. The platinum electrode was rotated at a constant speed of 810 r.p.m. and the titration potential (+0.20 volt, +0.60 volt, +0.60 volt and +0.70 volt for Ag, Au, Hg and Pd respectively) was applied to the indicator electrode. The metal was then titrated with a standard solution of thiosalicylamide (0.001*M*-0.05*M*), added through the third neck of the cell and the insoluble metal complex was precipitated. The titration was carried out until either the residual current (in case of Ag) or appreciable high current (in cases of Au, Hg and Pd) were recorded. The end points were obtained from the L-shaped (for Ag) or inversely L-shaped (for Au, Hg and Pd) titration curves (Fig. 2) after due correction due to volume changes. At +0.20 volt (vs. S.C.E), silver exhibits diffusion current on a platinum anode but the ligand is not oxidised. On the other hand, at about +0.60 volt (vs. S.C.E), gold, mercury and palladium are not electroactive but the ligand exhibits limiting current.

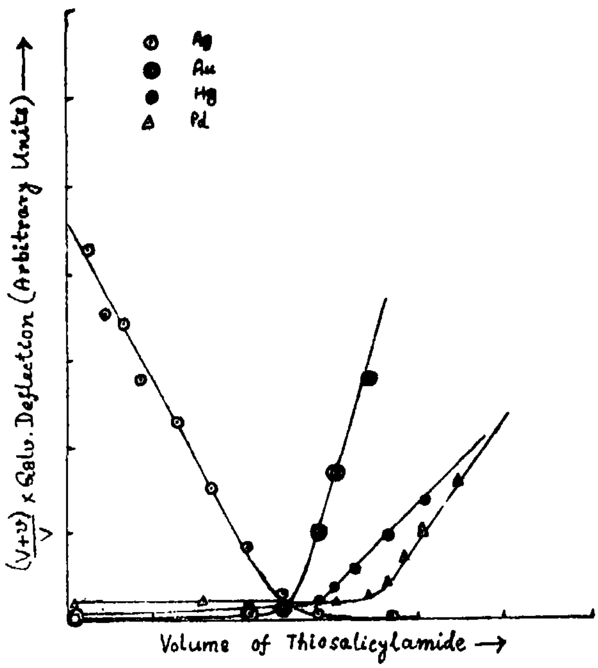


Fig. 2. Amperometric titration curves

For interference studies, known amounts of the foreign ions were added to a given amount of metal ion and the metal was titrated following the procedure as described above.

TABLE 1—AMPEROMETRIC DETERMINATION OF Ag(I), Au(III), Hg(II) AND Pd(II) WITH THIOSALICYLAMIDE

Ag taken (mg)	0.409	0.640	0.896	1.021	1.280	2.560	3.191
Ag found (mg)	0.400	0.630	0.890	1.030	1.280	2.560	3.250
Error (mg)	−0.009	−0.010	−0.006	+0.009	0.000	0.000	+0.059
Au taken (mg)	0.085	0.214	0.427	0.855	1.282	3.420	4.275
Au found (mg)	0.086	0.210	0.433	0.874	1.300	3.425	4.272
Error (mg)	+0.001	−0.004	+0.006	+0.019	+0.018	+0.005	−0.003
Hg taken (mg)	0.420	0.560	0.840	1.390	2.790	5 580	6.970
Hg found (mg)	0.370	0.520	0.850	1.360	2.780	5.600	7.200
Error (mg)	−0.050	−0.040	+0.010	−0 030	−0.010	+0.020	+0.230
Pd taken (mg)	0.071	0.115	0.230	0.460	0.920	1.170	1.860
Pd found (mg)	0.085	0.122	0.229	0.464	0.912	1.130	1.800
Error (mg)	+0.014	+0.007	−0.001	+0.004	−0.008	−0.040	−0.060

TABLE 2—AMPEROMETRIC DETERMINATION OF Ag(I), Au(III), Hg(II) AND Pd(II) WITH THIOSALICYLAMIDE IN PRESENCE OF DIVERSE IONS

Metals taken : 1.280 mg Ag, 0.855 mg Au, 2.790 mg Hg, 0.460 mg Pd

Diverse ion added	Ag found (mg)	Error (mg)	Au found (mg)	Error (mg)	Hg found (mg)	Error (mg)	Pd found (mg)	Error (mg)
Fe^{3+}	1.296 (8.00)	+0.016	0.861 (27.50)	+0.006	2.84 (34.46)	+0.05	0.461 (34.46)	+0.001
Co^{2+}	1.274 (6.40)	−0.006	0.867 (25.70)	+0.012	2.86 (20.99)	+0.07	0.460 (32.24)	0.000
Ni^{2+}	1.290 (6.20)	+0.010	0.857 (30.30)	+0.002	2.80 (38.06)	+0.01	0.458 (38.06)	−0.002
Cd^{2+}	1.274 (7.50)	−0.006	0.864 (15.00)	+0.009	2.82 (61.20)	+0.03	0.466 (45.00)	+0.006
Zn^{2+}	1.290 (9.00)	+0.010	0.864 (32.20)	+0.009	2.80 (22.64)	+0.01	0.461 (22.64)	+0.001
Pb^{2+}	1.285 (5.00)	+0.005	—	—	—	—	—	—
Al^{3+}	—	—	0.854 (16.10)	−0.001	2.84 (20.22)	+0.05	0.466 (20.22)	+0.006
Bi^{3+}	1.274 (17.00)	−0.006	—	—	—	—	—	—
Sb^{3+}	1.285 (12.50)	+0.005	—	—	2.82 (53.39)	+0.03	—	—
As^{3+}	1.30 (9.00)	+0.02	—	—	2.78 (41.32)	−0.01	—	—
Cr^{3+}	1.274 (5.20)	−0.006	0.861 (26.20)	+0.006	2.78 (32.80)	−0.01	0.466 (32.80)	+0.006
Mn^{2+}	1.285 (14.56)	+0.005	0.867 (35.00)	+0.012	2.85 (43.65)	+0.06	0.461 (43.65)	+0.001
V^{5+}	1.301 (10.00)	+0.021	0.854 (8.40)	−0.001	—	—	—	—
Zr^{4+}	—	—	0.861 (18.70)	+0.006	—	—	—	—
PO_4^{3-}	1.279 (26.53)	−0.001	—	—	2.86 (35.20)	+0.07	0.464 (35.20)	+0.004

N.B. The figure within parenthesis show the amount of foreign ion added, in mg.

Results and Discussion

The results of the amperometric determination of Ag(I), Au(III), Hg(II) and Pd(II) are shown in (Table 1). The metals can be estimated in presence of large amounts of different foreign ions as shown in Table 2. However, Cu(II), Tl(III), Se(IV), Te(IV) etc. interfere in the determination of the above four metals.

Accuracy and Precision :

The relative mean error and the coefficient of variation of Ag(I), Au(III), Hg(II) and Pd(II) estimations are calculated from ten experiments under identical conditions, using 1.280 mg Ag in 15 ml, 0.855 mg Au in 20 ml, 2.790 mg Hg in 16 ml and 0.460 mg Pd in 14 ml. The relative mean errors for Ag(I), Au(III), Hg(II) and Pd(II) are 0.078%, 0.935%, 1.362% and 0.434% respectively. The coefficient of variations for Ag(I), Au(III), Hg(II) and Pd(II) are 0.629%, 0.444%, 0.905% and 0.709% respectively.

Acknowledgement

The authors thank the University Grants Commission, New Delhi for providing financial assistance to AB and MM.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1159-1162

Infrared Spectra of Gaseous Acetylacetonates of Transition Metals

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Manuscript received 16 May 1980, accepted 25 August 1980

The IR spectra of the gaseous acetylacetonates of copper, aluminium, group 3A and some lanthanide metals are investigated in the frequency region 200-3500 cm^{-1}. The analysis of the spectral patterns suggests that copper acetylacetonate (hence written as $Cu(AA)_2$ where AA is the acetylacetonate anion) is a square-planar complex of D_{2h} symmetry and all the remaining $M(AA)_3$ chelates (M = Al, group 3A and lanthanide metals) belong to the D_3 symmetry group. The measurements of the metal-oxygen vibrations provide information on the M-O bond properties and on the stability of these molecules in the gas phase.

THE IR spectra of divalent and trivalent metals acetylacetonates have been the object of several theoretical and spectroscopic studies. Firstly Nakamoto[1] performed a normal-coordinate analysis on the $M(AA)_2$[1,2] and $M(AA)_3$[3] type complexes assuming a simplified 1 : 1 model. Subsequently Mikami[4] carried out a rigorous normal-coordinate treatment on the IR active vibrations of the 1 : 2 and 1 : 3 chelates. These calculations provided a more detailed assignment of the IR spectra. The results of ^{13}C and ^{18}O experiments[5,6] allowed the assignment of the CO and CC stretchings, the nature of which has been a subject of controversy. At last, measurements of the metal isotope shifts on the metal-ligand vibrations[7] have proved an instrument to characterize the motions involving the metal atom.

However, up to now, the spectroscopic studies carried out on these complexes are available for the solid phase and for liquid solutions and little information was drawn in the low IR region. The aim of this systematic study of the IR spectra of a series of acetylacetonates is to provide a detailed analysis of their spectral features and to achieve their structural and bonding properties in the gas phase. Moreover, the measurements of the metal-oxygen vibrations can be employed to characterize the M – O bond and to foresee the stability of these complexes in the gas phase.

Experimental

The IR spectra were recorded between 200 cm^{-1} and 3500 cm^{-1} by using a Perkin-Elmer IR grating spectrophotometer model 180. The samples were vaporized at ca. 400 K in a pyrex cell, 30 cm path length, heated by a Kanthal wire. The temperature of the furnace was measured by an iron-constantan thermocouple. The cell was filled with nitrogen at one atm. as a gas diffusion barrier and to avoid the condensation of the vapors on the optical windows. Various scannings were run before and after each experiment in order to distinguish between the background, vapors condensed on the optical windows by chance and the absorptions due to the wished species. Copper and aluminium acetylacetonates were synthetized according to the standard methods[8]; the remaining compounds were highly pure commercial products supplied by the Research Org.-Inorg. Chem. Co. They were purified following the procedure reported in the literature[8] and outgassed under vacuum for several hours.

Results and Discussion

The IR spectra of the gaseous chelates show a similar spectral pattern consisting of a series of bands which do not suffer the substitution of the metal atom and of some bands which are sensitive to the mass of the metal. The former are therefore related to the vibrations of the acetylacetonate anion and the latter to the motions involving the metal-oxygen bonds. The analysis of these spectra is based on the assumption that the D_{2h} symmetry is held by $Cu(AA)_2$ according to the crystallographic data[9,10] and that the $M(AA)_3$ type chelates belong to the D_3 symmetry group by analogy with the structure of $Fe(AA)_3$[11]. The description of the normal vibrations expected in case of the acetylacetonates of divalent and trivalent metals are summarized in Table 1. The assignment of the bands observed in this study are considerably aided by comparing our measurements with previous investigations on these complexes[1-6] and taking into account the results of normal-coordinate treatments[1,3,4]. The conclusions based on ^{18}O and

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^{13}C isotopic shifts[5,6] and on the metal isotope effects on the metal-ligand vibrations[7] have been considered as well.

The bands observed in the IR spectra of gaseous $Cu(AA)_2$, $Al(AA)_3$ and $Sc(AA)_3$ are promptly attributed to the above mentioned species on the basis of recent thermodynamic studies[12,13] which indicate that these species are stable in the gas phase. The comparison among all the spectra suggests that the bands observed in the remaining complexes [except $Cu(AA)_2$] must belong to the $M(AA)_3$ gaseous species. Owing to the close similarity of the spectra of the acetylacetonates of the trivalent metals, we restrict the discussion of the spectral features to copper and aluminium acetylacetonates for sake of brevity.

The absorptions ranging between 2850 cm^{-1} and 3060 cm^{-1} are confidently attributed to the CH_3 and CH stretchings and further discussions are needless; likewise, the bands around 1410 cm^{-1} and 1390 cm^{-1} belong to the CH_3 deformations. A number of bands is present in all the spectra between 1530 cm^{-1} and 1580 cm^{-1} where the CO and CC stretching vibrations are expected. Nakamoto[1] based the assignment of these bands on the ground of normal-coordinate calculations; these modes were found slightly coupled with each other[4], however, ^{13}C and ^{18}O isotopic substitution[5,6] indicates that the CO stretching occurs at a higher frequency than the CC vibration. The IR spectra of solid acetylacetonates[2-4] show a band around 1550 cm^{-1} which *Mikami*[4] *assigned to a combination mode while* Pinchas[6] assigned it to the symmetric CO stretching. According to the results of the vibrational analysis reported in Table 1, two IR active vibrations are expected both for the CO and CC stretchings under the D_{2h} symmetry and three IR active modes are foreseen for the same vibrations in case of the 1 : 3 chelates. These expectations are completely fulfilled since the spectrum of $Cu(AA)_2$ shows peaks at 1583 cm^{-1} and 1560 cm^{-1} which we assign to the CO stretchings of B_{2u} and B_{1u} symmetry species respectively while the CC stretching of B_{2u} symmetry should correspond to the band at 1527 cm^{-1}. As regards the assignment of these *vibrations for the* 1 : 3 *complexes, the spectrum of* $Al(AA)_3$, *for instance, reveals absorptions at* 1580, 1570, and 1560 cm^{-1} assigned to the CO stretchings while the bands at 1543 and 1532 cm^{-1} to the CC stretchings of E symmetry. The remaining CC stretching of B_{1u} species is identified in the band at 1281 cm^{-1} in case of $Cu(AA)_2$ and that of E type at 1288 cm^{-1} for $Al(AA)_3$. The assignment of these latter bands is based on the conclusions carried out by several authors[1,4] and confirmed by ^{18}O isotopic shift measurements[6] which also suggest the coupling of this vibration with the CR stretching ($R—CH_3$). The band falling around 1190 cm^{-1} in all the spectra is assigned to the CH in-plane deformation as supported by deuteration[4]. The respective out-of-plane deformation corresponds to the absorption at 786 cm^{-1} (B_{3u}) which appears in the spectrum of $Cu(AA)_2$ and at 803 cm^{-1}(E) and 783 cm^{-1}(A_2) in the spectrum of $Al(AA)_3$. Particularly interesting is the assignment of the CR stretchings. The vibrational analysis foresees two IR active modes (B_{1u} and B_{2u}) in the square-planar complex and three IR frequencies (A_2 and 2E) for the 1 : 3 chelates. Normal-coordinate treatments[1-4] provide the position of the corresponding frequencies, however, both the spectra of the divalent[1,2,4] and trivalent[3,4] metals acetylacetonates recorded in the solid phase show only one band lying between 930-940 cm^{-1}. These motions should be coupled with the CO stretching as suggested by ^{18}O and ^{13}C experiments[5,6].

TABLE 1—ANALYSIS OF THE NORMAL VIBRATIONS OCCURRING IN THE 1 : 2 AND 1 : 3 CHELATES

$Cu(AA)_2$, D_{2h} symmetry	
Cu – O, C – O, C – C and C – R(a) stretchings	A_g, B_{3g}, B_{1u}, B_{2u}
C – H stretchings	A_g, B_{1u}
Ring in-plane deformations	$2A_g$, $2B_{3g}$, $2B_{1u}$, $2B_{2u}$
C – R(a) in-plane deformations	A_g, B_{1g}, B_{1u}, B_{2u}
C – H in-plane deformations	B_g, B_{2u}
Ring out-of-plane deformations	$3B_{2g}$, $3B_{3u}$, $2A_u$
C – R(a) out-of-plane deformations	$2B_{1g}$, A_u, B_{3u}
C – H out-of-plane deformations	B_{2g}, B_{3u}
$M(AA)_3$ type chelates, D_3 symmetry	
M – O, C – O, C – C and C – R(a) stretchings	A_1, A_2, 2E
C – H stretchings	A_1, E
Ring in-plane deformations	$2A_1$, $5A_2$, 6E
C – H in-plane deformations	A_1, E
Ring out-of-plane deformations	$3A_1$, $2A_2$, 6E
C – H out-of-plane deformations	A_2, E

(a) $R=CH_3$

Particular emphasis is reserved to the absorptions below 700 cm^{-1} where the ring deformations and the M – O vibrations fall. Several modes lying here are coupled with each other[4,7] The absorptions around 690 cm^{-1} and 660 cm^{-1} attributed to a planar ring deformation and to the CR bending respectively, both coupled with the M – O stretching as confirmed by metal isotope shifts measurements[7]. The out-of-plane ring deformation is assigned to the bands observed at 614 cm^{-1} and at 584 cm^{-1} in case of $Cu(AA)_2$ and $Al(AA)_3$ respectively; this vibration should contain a small amount of M – O stretching character[2-4,8]. In case of $Cu(AA)_2$ two IR active Cu – O stretchings of B_{1u} and B_{2u} symmetry are foreseen (see Table 1). The B_{1u} vibration is identified in the absorption at 468 cm^{-1} which should be coupled with the CR stretching according to the conclusions of Mikami[4] and Nakamoto[7]. The remaining Cu – O stretching of B_{2u} species should fall around 300 cm^{-1} [4,6] and it can be reliably recognized in the band at 293 cm^{-1}. As concerns the M – O stretching modes occurring in the 1 : 3 chelates, three of them are IR active under the D_3 symmetry (A_2 and 2E). According to the normal-coordinate calculations[3,4], the peak

which we observe at 495 cm^{-1} in the spectrum of $Al(AA)_3$ corresponds to one of the degenerate Al – O stretchings ; the A_2 and the other E vibrations are identified in the absorptions at 370 and 238 cm^{-1} respectively.

One of the most remarkable differences among the spectra of the $M(AA)_3$ and $Cu(AA)_2$ complexes is the presence of a strong absorption around 535 cm^{-1} which only appears in the spectra of the former chelates. This band corresponds to the frequency at 515 cm^{-1} of the enol form of acetylacetone[14] and according to the previous investigations it is assigned to a ring planar deformation, coupled with the M – O stretching[6,15]. A series of absorptions are detected in the spectra of copper and of the remaining acetylacetonates in the far IR region. The bands at 293, 268 and 219 cm^{-1} most probably are related to the bands at 291, 268 and 217 cm^{-1} observed in the spectrum of solid $Cu(AA)_2$[4]. In this region we observe a further line at 210 cm^{-1} ; this band, never observed up to now, could correspond to that calculated by Mikami[4] at 207 cm^{-1} and which we assign to a in-plane ring deformation. As regards the investigation of this range in the case of the trivalent metals acetylacetonates, the only available assignment reported in the literature is that proposed by Mikami[4] for $Fe(AA)_3$. The IR spectra of solid $Al(AA)_3$[3,15], $La(AA)_3$[15] and $Nd(AA)_3$[15] do not show the presence of absorptions below 370 cm^{-1}. Our gas phase spectra, however, display peaks at 270, 238, 215 and 207 cm^{-1} which have been assigned according to the normal-coordinate analysis of Nakamoto[3] and Mikami[4]. It must be pointed out that some vibrations as the CR in-plane deformations and few other ring deformations occurring in the 1 : 3 chelates are expected at frequencies very close to each other[1-4] so that the broadness of the corresponding absorptions does not allow to reveal such bands.

Conclusions :

The analysis of the IR spectra of the gaseous acetylacetonates of copper and of the trivalent transition metals indicates that some differences mark the spectra of the $M(AA)_3$ chelates from the $Cu(AA)_2$ complex as a different number of absorptions related to the CO, CC and CR stretchings and for the presence of a characteristic band ranging around 530 cm^{-1} in the 1 : 3 chelates. The spectroscopical expectations for the 1 : 2 and 1 : 3 complexes are in each case completely fulfilled.

The measurements of the shift of the band at 515 cm^{-1} of the enol form of acetylacetone[14] upon complexing and of the M – O stretching frequency (T-that at the highest wavenumber) were taken into account by some investigators[1,15] to characterize the nature of the M – O bond and to foresee the stability of these complexes. It seems therefore natural to us to extend this study to the gaseous acetylacetonates on the basis of our measurements carried out in the gas phase. Measurements of the M – O vibrations are particularly suitable to achieve directly this kind of information as the strength of the M – O bond and the stability of the chelate. The M – O stretching frequencies occur at 495 cm^{-1} and at 468 cm^{-1} in the gaseous acetylacetonates of aluminium and copper, the corresponding frequencies measured for the solid phase are 490 and 455 cm^{-1} respectively. Nakamoto[3] concluded by comparing the calculated force constants that the Cu – O bond has a partial double bond character and that the Al – O bond is strongly covalent. The present results suggest that the same conclusions can be drawn for the gaseous $Al(AA)_3$ and $Cu(AA)_2$ complexes as well. In order to put forward conclusions on the M – O bond character for the remaining complexes, the values of the highest M – O frequencies were plotted versus LogM (M = mass of the metal atom in a.m.u.). These frequencies follow a linear trend and the corresponding νAl – O was found to be aligned with them (see Fig. 1). The trend observed most probably reflects the change in mass of the metal suggesting therefore that the M – O force

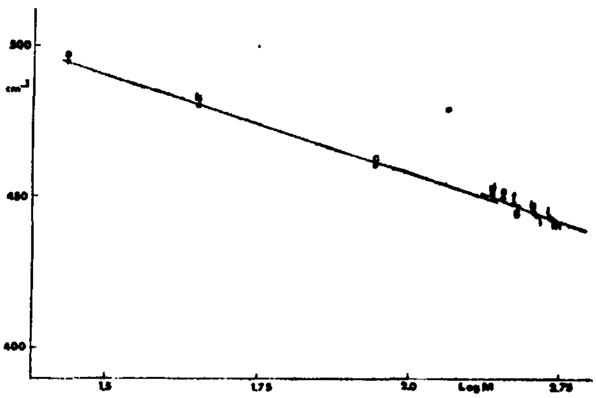


Fig. 1. Plot of the experimental M – O frequencies (cm^{-1}) versus LogM for the $M(AA)_3$ type chelates ; (the LogM scale above 2.0 is different from that below 2.0) : a = Al, b = Sc, c = Y, d = La, e = Nd, f = Sm, g = Eu, h = Dy, i = Ho, l = Yb and m = Lu.

constants are approximataly the same for all the 1 : 3 chelates and quite close to that of the Al – O bond[3]. This behavior should indicate that the M – O bond character in Sc, Y, La and in the lanthanides is as covalent as that of the Al – O bond. On this ground, we have derived two sets of linear equations, one including the νAl – O, νSc – O, νY – O and νLa – O frequencies and another including the remaining νM – O frequencies (M = Nd, Sm, Eu, Dy, Ho, Yb and Lu) which correlate the highest νM – O values to LogM. The least-squares treatment yields for the former set the following straight line : $\bar{\nu}$ (cm^{-1}) = 586 – 64 LogM and for the latter one the equation : $\bar{\nu}$ (cm^{-1}) = 584 – 63LogM. Our conclusions seem to be strengthened by the insignificant shifts measured for the band at 515 cm^{-1} of the enol form of acetylacetone[14] which ranges from 535 cm^{-1} to

531 cm^{-1} passing from $Al(AA)_3$ to $Lu(AA)_3$. On this basis we foresee the same stability of gaseous $Al(AA)_3^{+}$ for the gaseous $M(AA)_3$ type chelates.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1163-1165

Syntheses of Furano Compounds. Part XLV Syntheses of 1-Oxo-1H-Benzo[b]Furo[4,3-d]Indeno [2′,1′ : 5,6]Pyrans and Nitrogen Analogues

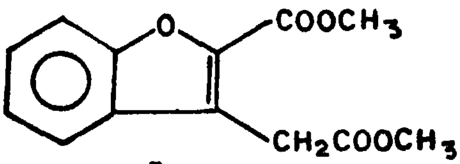
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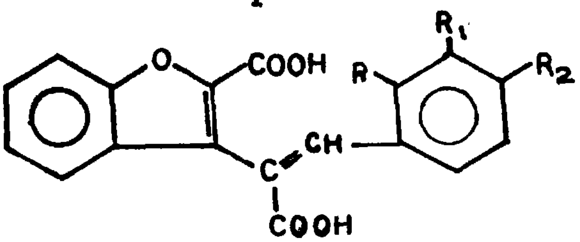
Manuscript received 23 October 1979, revised 18 June 1980, accepted 29 October 1980

It is shown that cyclisations of α-benzyl-2-carboxybenzo[b]-furan-3-acetic acids lead to formation of the corresponding 1-oxo-1H-benzo[b]furo[4,3-d]indeno[2′, 1′ : 5,6] pyrans. Some reactions of these pyrones have been studied.

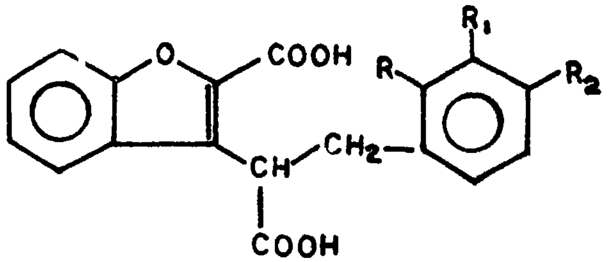
METHYL 2-methoxycarbonylbenzo [b] furan-3-acetate[1](I) underwent Stobbe condensation[2] with aromatic aldehydes in alcoholic sodium methoxide leading to benzylidenedicarboxylic acids (II-V). These acids were characterised by corresponding anhydrides which were readily obtained on treatment with acetic anhydride. On reduction, the Stobbe products afforded the dihydro derivatives (VI-IX).



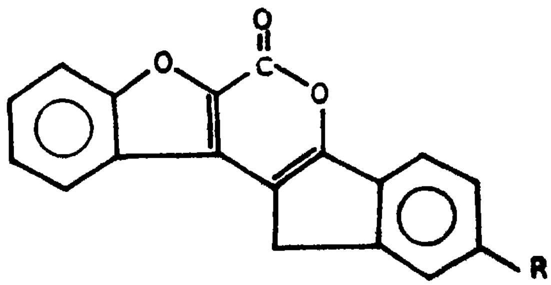
I



(II) $R = R_1 = H, R_2 = CH_3$
(III) $R_1 = R_2 = H, R = OCH_3$
(IV) $R = R_2 = H, R_1 = OCH_3$
(V) $R = R_1 = R_2 = H$



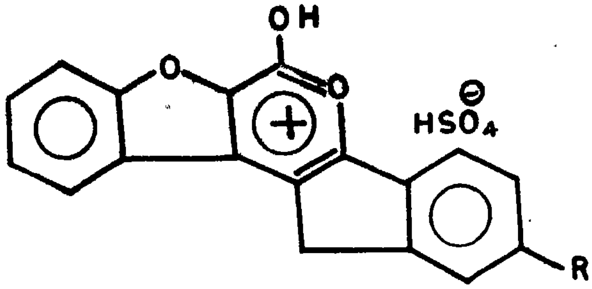
(VI) $R = R_1 = H, R_2 = CH_3$
(VII) $R_1 = R_2 = H, R = OCH_3$
(VIII) $R = R_2 = H, R_1 = OCH_3$
(IX) $R = R_1 = R_2 = H$



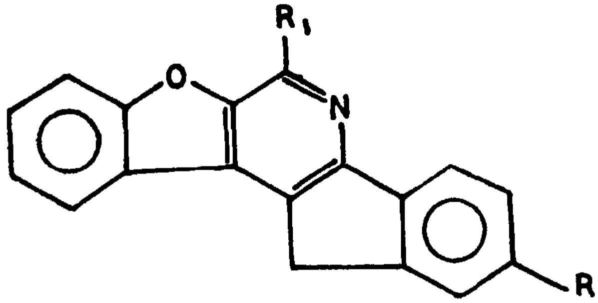
(X) $R = OCH_3$
(XI) $R = H$

The compound (IX) on treatment with polyphosphoric acid underwent cyclodehydration and lactonisation giving the indenopyrone[3] (X and XI) ($\nu_{C=O}$ 1725 cm^{-1}) which showed a brilliant violet fluorescence in sulphuric acid due to the formation of 1-hydroxyisobenzo[b]furopyrylium salt (XIII). The cyclodehydration of (VIII) led to the formation of a single product which was assigned the structure (X)[4].

The pyrones (X and XI) on treatment with alcoholic ammonia[5] afforded the related α-pyridones(XIV and XV). On treating(XV) with phosphorus oxychloride and phosphorus pentachloride[6], the chloro compound(XVI) was obtained (phosphorus oxychloride alone was ineffective) which was catalytically dechlorinated to (XVII).



(XII) R=OCH_3
(XIII) R=H



(XIV) R_1=OH, R=OCH_3
(XV) R_1=OH, R=H
(XVI) R_1=Cl, R=H
(XVII) R=R_1=H

Experimental

All melting points are uncorrected. The IR spectra were determined in KBr pellet in Perkin-Elmer Spectrophotometer Model 237.

α-p-Methylbenzylidene-2-carboxybenzo[b]furan-3-acetic Acid(II):

A mixture of *p*-tolualdehyde (0.12 g) and methyl 2-methoxycarbonylbenzo[b] furan-3-acetate(I) (0.25 g) was added to a solution of sodium (0.03 g) in dry methanol (2 ml) and the mixture refluxed for 6 hrs. Solvent was then removed under reduced pressure to afford a colourless solid which was washed with ether, boiled with NaOH (1.5 ml; 10%) for 1.5 hrs and then acidified (conc. HCl) to furnish (II) which crystallised from aqueous acetic acid in colourless needles, m.p. 270° (decomp). (Found: C, 70.76; H, 4.29. $C_{19}H_{14}O_5$ requires C, 70.80; H, 4.38%). The related anhydride was obtained by heating(II) with acetic anhydride, crystallised from acetic anhydride in glittering yellow needles, m.p. 209°. (Found: C, 74.96; H, 3.86. $C_{19}H_{12}O_4$ requires C, 74.99; H, 3.97%); ν_{max} 1750 and 1780 cm^{-1}.

Reduction of (II) with Sodium Amalgam:

The compound(II) (0.55 g) was dissolved in 10% NaOH solution and reduced with sodium amalgam (22.0 g; 2%) for 48 hrs. The aqueous layer was filtered and acidified (conc. HCl) and extracted with ether. The ether solution was washed with water and dried (Na_2SO_4). Removal of ether afforded the benzyl compound(VI) as a thick viscous oil (0.5 g). (Found: C, 70.28; H, 4.89. $C_{19}H_{16}O_5$ requires C, 70.36; H, 4.98%).

α-o-Methoxybenzylidene-2-carboxybenzo[b] furan-3-acetic Acid(III):

Compound(I) and *o*-methoxybenzaldehyde similarly gave(III) in colourless small needles from aqueous acetic acid, m.p. 224° (decomp). (Found: C, 67.41; H, 4.08. $C_{19}H_{14}O_6$ requires C, 67.45; H, 4.17%); ν_{max} 1675 and 1700 cm^{-1}. The related anhydride was obtained in yellow needles from acetic anhydride, m.p. 224°. (Found: C, 71.10; H, 3.61. $C_{19}H_{12}O_5$ requires C, 71.25; H, 3.78%).

The dihydro derivative(VII) was similarly obtained on reduction as a colourless viscous oil. (Found: C, 66.91; H, 4.71. $C_{19}H_{16}O_6$ requires C, 67.05; H, 4.75%).

α-m-Methoxybenzylidene-2-carboxybenzo[b] furan-3-acetic Acid(IV):

This was obtained from (I) and *m*-methoxybenzaldehyde as before in colourless shining plates from aqueous acetic acid, m.p. 228° (decomp). (Found: C, 67.45; H, 4.21. $C_{19}H_{14}O_6$ requires C, 67.45; H, 4.17%); ν_{max} 1685 and 1710 cm^{-1}.

The corresponding anhydride was obtained in yellow plates from acetic anhydride, m.p. 197°. (Found: C, 71.18; H, 3.62. $C_{19}H_{12}O_5$ requires C, 71.25; H, 3.78%).

The dihydro derivative(VIII) was obtained as a colourless viscous oil. (Found: C, 66.96; H, 4.72. $C_{19}H_{16}O_6$ requires C, 67.05; H, 4.75%).

1-Oxo-1H-5'-methoxybenzo[b] furo[4,3-d]indeno [2',1' : 5,6] pyran:

The benzyl compound (VIII, 0.55 g) was heated with polyphosphoric acid (25.1 g) at 120-30° for 5 hrs. The resulting mass was poured over crushed ice and stirred when a black product separated. This was extracted with benzene; the benzene layer washed successively with aqueous $NaHCO_3$, water and dried ($MgSO_4$). Removal of benzene gave a yellow solid which crystallised from acetic acid in yellowish brown needles (0.23 g), m.p. 233°. (Found: C, 74.82; H, 3.87. $C_{19}H_{12}O_4$ requires C, 74.99; H, 3.97%); ν_{max} 1741 cm^{-1}.

The compound dissolved in conc. H_2SO_4 giving yellow colour and imparting brilliant green fluorescence.

1-Oxo-1H, 2H-5'-methoxybenzo [b] furo [4,3-d] indeno [2',1' : 5,6]-pyridine(XIV) :

The foregoing compound (0.1 g) was taken in a sealed tube with alcoholic ammonia (5 ml ; saturated at 0°) and heated at 140° for 5 hrs. It was then cooled to furnish brown crystals of (XIV) in quantitative yield which crystallised from acetic acid in light yellowish brown crystalline solid, m.p. >300°. (Found : N, 4.56. $C_{19}H_{13}O_3N$ requires N, 4.62%) ; ν_{max} 1665 cm^{-1}.

α-Benzylidene-2-carboxybenzo [b] furan-3-acetic Acid(V) :

Compound(I) on Stobbe condensation with benzaldehyde similarly gave (V) in colourless shining granules from aqueous acetic acid, m.p. 248° (decomp). (Found : C, 70.11 ; H, 3.67. $C_{18}H_{12}O_5$ requires C, 70.13 ; H, 3.92%) ; ν_{max} 1698 and 1720 cm^{-1}.

The related anhydride was obtained as orange shining needles from acetic anhydride, m.p. 207°. (Found : C, 74.41 ; H, 3.35. $C_{18}H_{10}O_4$ requires C, 74.48 ; H, 3.47%).

The benzyl compound(IX) was obtained on reduction as colourless thick oil. This was treated with polyphosphoric acid without purification.

1-Oxo-1H-benzo[b] furo [4,3-d] indeno [2',1' : 5,6] pyran (XI) :

The foregoing oil (0.2 g) was heated with polyphosphoric acid (10.0 g) at 120-30° for 12 hrs. On working up, (XI) was obtained which crystallised from benzene in yellow needles, m.p. 267°. (Found : C, 78.76 ; H, 3.60. $C_{18}H_{10}O_3$ requires C, 78.82 ; H, 3.68%) ; ν_{max} 1725 cm^{-1}. The compound showed a brilliant violet fluorescence in conc. H_2SO_4.

1-Oxo-1H, 2H-benzo [b] furo [4,3-d] indeno [2',1' : 5,6] pyridine(XV) :

The pyrone (XI, 0.1 g) was heated at 140° with ethanolic ammonia (5 ml, saturated at 0°) in a sealed tube for 5 hrs. On working up, yellowish brown crystals of the pyridine(XV) were obtained from acetic acid, m.p. >370°. (Found : C, 79.06 ; H, 3.90 ; N, 5.04. $C_{18}H_{11}O_2N$ requires C, 79.11 ; H, 4.06 ; N, 5.13%) ; ν_{max} 1660 cm^{-1}.

1-Chlorobenzo[b] furo [4,3-d] indeno [2',1' : 5,6] pyridine(XVI) :

A mixture of foregoing compound (0.05 g), $POCl_3$ (1.5 g) and PCl_5 (1.5 g) was heated at 165-70° for 6 hrs. The resulting mixture was cooled, poured over crushed ice, basified with ammonia and extracted with chloroform. The dried chloroform solution was filtered through an alumina column and the filtrate concentrated to afford colourless crystals. It crystallised from benzene-petroleum ether in prisms, m.p. 216-17°. (Found : C, 73.81 ; H, 3.30. $C_{18}H_{10}ONCl$ requires C, 74.09 ; H, 3.43%).

Benzo [b] furo [4,3-d] indeno [2',1' : 5,6] pyridine (XVII) :

The foregoing chloro compound (0.05 g) in methanol was hydrogenated at room temperature in presence of KOH (0.03 g) using palladised charcoal (0.05 g ; 10%). Absorption of hydrogen was complete in a few minutes. The mixture was filtered, the filtrate concentrated and diluted with water and extracted with ether ; the ether solution washed with water and dried (Na_2SO_4). Removal of the solvent afforded a yellow oil. The compound gave a dull yellow picrate which crystallised from alcohol in light yellow crystals, m.p. 189-90°. (Found : C, 59.39 ; H, 2.79 ; N, 11.51. $C_{18}H_{11}ON.C_6H_3O_7N_3$ requires C, 59.46 ; H, 2.88 ; N, 11.52%).

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Vol. LVII, December 1980, pp. 1166-1169

A Novel Route to the Synthesis of 3-Arylimino-5-Substituted-1,2,4-Dithiazoles. Part I : Oxidative Debenzylation and Cyclisation of S-Benzyliso-N-Arylthiocarbamoyl-Thioacetamides

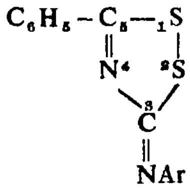
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Manuscript received 26 September 1977, revised 12 June 1978, accepted 29 October 1980

A novel route to the synthesis of 3-phenylimino-5-methyl-, 3-p-Cl-phenylimino-5-methyl-, 3-p-tolylimino-5-methyl- and 3-p-methoxyphenylimino-5-methyl-1,2,4-dithiazoles, through the oxidative debenzylation and cyclisation of the corresponding S-benzyliso-N-arylthiocarbamoyl-thioacetamides, has been described.

ALTHOUGH a number of 3-imino-5-substituted-imino-, 3, 5-disubstitutedimino- and 3-substituted-imino-5-disubstitutedamino-1,2,4-dithiazolidines/dithiazolines have been prepared by various methods[1-11], only a few 3-arylimino-5-aryl-1,2,4-dithiazoles (I), obtained by the interaction of thiobenzamide and aryliminochloromethane-sulphenyl-chloride, have been reported[12].



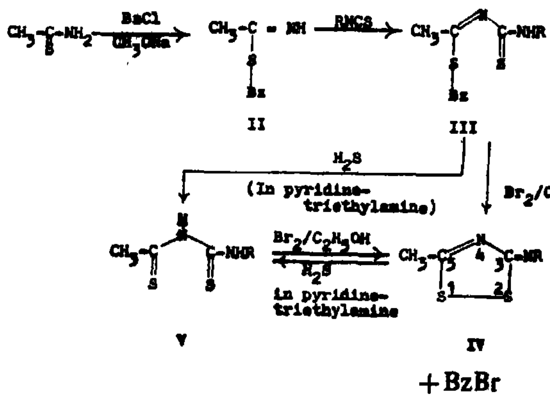
I

In view of the reported low yields of these 1, 2, 4-dithiazoles and with the object of investigating the possibility of oxidative debenzylation and cyclisation reaction in S-benzylisothiamide system, it was considered worthwhile to search for an alternative route of synthesis for this new class of compounds.

The present communication reports a novel route to the synthesis of 3-arylimino-5-methyl-1, 2, 4-dithiazoles (IV) through the oxidative debenzylation and cyclisation of S-benzyliso-N-arylthiocarbamoyl-thioacetamides(III).

Following Werner's procedure[13], thioacetamide was benzylated with benzylchloride in presence of sodium methoxide. The expected S-benzylisothioacetamide(II) was condensed with appropriate arylisothiocyanate. The reaction afforded the desired S-benzyliso-N-arylthiocarbamoyl-thioacetamides(III), which on oxidation with bromine in chloroform solution, resulted in the formation of a debenzylated and cyclised product, 3-arylimino-5-methyl-1, 2, 4-dithiazoles (IV). The structure of IV was finally settled, as they were also obtained by the direct oxidation of the related N-arylthiocarbamoyl-thioacetamides (V). V were obtained by the reductive debenzylation of the corresponding S-benzyliso-N-arylthiocarbamoyl-thioacetamides(III) with dry hydrogen sulphide in pyridine-triethylamine solution[14] and also by reduction of the related dithiazole(IV) under identical conditions. Compounds IV and V were characterised by the elemental analysis, mixture melting point technique and identical IR spectra.

The scheme of the reactions can be represented as follows :



where R = phenyl-, *p*-tolyl-, *p*-Cl-phenyl- or *p*-methoxyphenyl group
Bz = benzyl group.

Experimental

Melting points were determined in capillary tubes. Infrared spectra were recorded in Nujol on a Perkin-Elmer Spectrophotometer (Model-720).

S-Benzyliso-thioacetamides(II) : Thioacetamide (5 g) was benzylated with benzyl chloride (8.5 ml) in methanol (20 ml) in presence of sodium methoxide (3.75 g). The reaction mixture was stirred for 3 hrs and was allowed to stand overnight. It was then refluxed for about 15 minutes. Excess of the solvent was evaporated and the resulting product was extracted with benzene and dried over anhydrous calcium chloride. Evaporation of excess benzene, afforded the desired S-benzyliso-thioacetamide(II), which was crystallised from ethanol, m.p. 48°, (yield 65%).

S-Benzyliso-N-arylthiocarbamoyl-thioacetamides(III) : The details of a typical experiment are as follows :

S-Benzylisothioacetamide(II) (5 g) was refluxed with phenylisothiocyanate (4.2 ml) and 15 ml of sodium hydroxide (10%) for 30 minutes. The semi-solid product was extracted with benzene and the extract further refluxed for 30 minutes. The resulting mass obtained, on evaporation of the solvent, was washed with petroleum ether (40 – 60°) and then treated with ethanol to afford the expected S-benzyliso - N - phenylthiocarbamoyl - thioacetamide(III) which was crystallised from ethanol, m.p. 128°, (yield 72%).

These results are summarised in Table 1.

3-Arylimino-5-methyl-1, 2, 4-dithiazoles(IV) :

(*i*) *Oxidative debenzylation and cyclisation of S-benzyliso-N-arylthiocarbamoyl-thioacetamides(III)* : Details of a representative experiment are as

TABLE 1—S-BENZYLISO-N-ARYLTHIOCARBAMOYL-THIOACETAMIDES

Reactants	S-benzyliso-N-arylthiocarbamoyl-thioacetamides formed	Yield %	M.P. °C	Formula	Analysis Found	Reqd.
Phenylisothio-cyanate+SBT	S-benzyliso-N-phenylthio-carbamoyl-T	72	128	$C_{16}H_{16}N_2S_2$	N : 9.07 S : 22.04	9.83 21.88
p-Cl-phenyliso-thiocyanate+SBT	S-benzyliso-N-*p*-Cl-phenylthio-carbamoyl-T	69	140	$C_{16}H_{15}N_2S_2Cl$	N : 8.54 S : 20.40	8.87 19.14
p-tolylisothio-cyanate+SBT	S-benzyliso-N-*p*-tolylthio-carbomoyl-T	65	145	$C_{17}H_{18}N_2S_2$	C : 65.38 H : 5.79 N : 8.31	64.96 5.73 8.91
p-methoxyphenyl-isothiocyanate+SBT	S-benzyliso-N-*p*-methoxyphenyl-thiocarbamoyl-T	63	195	$C_{17}H_{18}N_2S_2O$	N : 8.62 S : 19.50	8.48 19.39

SBT—denotes S-benzylisothioacetamide,
T—denotes thioacetamide.
Characteristic IR frequencies (cm^{-1}) of S-Benzyliso-N-phenylthiocarbamoyl-thioacetamide :
3210m, NH stretching (Lit[16] 3400-3100), 1160m, 1170w, 1195w, $N-C(=S)-N$ grouping (Lit[16] 1200-1600).

TABLE 2—3-ARYLIMINO-5-METHYL-1,2,4-DITHIAZOLES : OXIDATIVE DEBENZYLATION AND CYCLISATION OF S-BENZYLISO-N-ARYLTHIOCARBAMOYL-THIOACETAMIDES

S-Benzyliso-N-arylthiocarbamoyl-thioacetamide oxidised	3-Arylimino-5-methyl-1,2,4-dithiazole formed	Yield %	M.P. °C	Formula	Analysis Found	Reqd.
S-Benzyliso-N-phenyl-TT	3-phenylimino-5-methyl-DT	65	158	$C_9H_8N_2S_2$	N : 13.28 S : 31.08	13.46 30.76
S-benzyliso-N-*p*-Cl-phenyl-TT	3-*p*-Cl-phenyl-imino-5-methyl-DT	60	194	$C_9H_7N_2S_2Cl$	C : 45.30 H : 3.01 N : 11.70 S : 26.20	44.53 2.88 11.54 26.39
S-benzyliso-N-*p*-tolyl-TT	3-*p*-tolylimino-5-methyl-DT	68	162	$C_{10}H_{10}N_2S_2$	C : 53.84 H : 4.20 N : 12.84 S : 29.12	54.05 4.50 12.61 29.00
S-benzyliso-N-*p*-methoxyphenyl-TT	3-*p*-methoxyphenylimino-5-methyl-DT	63	145	$C_{10}H_{10}N_2S_2O$	N : 12.08 S : 26.66	11.77 26.89

TT—denotes thiocarbamoyl-thioacetamide,
DT—denotes 1,2,4-dithiazole,
Characteristic IR frequencies (cm^{-1}) of 3-phenylimino-5-methyl-1,2,4-dithiazole : Ring $-C-S$ (1070m)[16], $C=N$ (1620s)[16], ring $-S-S-$ linkage (490m)[16].

TABLE 3—3-ARYLIMINO-5-METHYL-1,2,4-DITHIAZOLES : OXIDATION OF N-ARYLTHIOCARBAMOYL-THIOACETAMIDES WITH BROMINE IN DILUTE ETHANOL

N-Arylthiocarbamoyl-thioacetamide oxidised	3-Arylimino-5-methyl-1,2,4-dithiazole formed	Yield %	M.P. °C	Formula	Analysis Found	Reqd.
N-phenylthio-carbamoyl-T	3-phenylimino-5-methyl-DT	70	157	$C_9H_8N_2S_2$	N : 13.23	13.46
					S : 30.48	30.76
N-*p*-Cl-phenyl-thiocarbamoyl-T	3-*p*-Cl-phenyl-imino-5-methyl-DT	65	194	$C_9H_7N_2S_2Cl$	N : 10.98	11,54
					S : 27.01	26.39
N-*p*-tolylthio-carbamoyl-T	3-*p*-tolylimino-5-methyl-DT	75	163-64	$C_{10}H_{10}N_2S_2$	C : 54.78	54.05
					H : 4.98	4.50
					N : 12.42	12.61
N-*p*-methoxy-phenylthiocarbamoyl-T	3-*p*-methoxy-phenylimino-5-methyl-DT	73	145	$C_{10}H_{10}N_2S_2O$	N : 12.25	11.77
					S : 26.56	26.89

T—denotes thioacetamide,
DT—denotes 1,2,4-dithiazole.

TABLE 4—N-ARYLTHIOCARBAMOYL-THIOACETAMIDES : REDUCTIVE DEBENZYLATION OF S-BENZYLISO-N-ARYLTHIOCARBAMOYL-THIOACETAMIDES WITH HYDROGEN SULPHIDE IN PYRIDINE-TRIETHYLAMINE MEDIUM

S-Benzyliso-N-arylthiocarbamoyl-thioacetamide reduced	N-Arylthiocarbamoyl-thioacetamide formed	Yield %	M.P. °C	Formula	Analysis Found	Reqd.
S-benzyliso-N-phenyl-TT	N-phenylthio-carbomoyl-T	82	148	$C_9H_{10}N_2S_2$	C : 52.08	51.42
					H : 4.79	4.76
					N : 14.03	13.33
S-benzyliso-N-*p*-Cl-phenyl-TT	N-*p*-Cl-phenyl-thiocarbamoyl-T	78	160	$C_9H_9N_2S_2Cl$	N : 10.96	11.45
					S : 26.52	26.17
S-benzyliso-N-*p*-tolyl-TT	N-*p*-tolylthio-carbamoyl-T	86	152	$C_{10}H_{12}N_2S_2$	N : 11.71	12.50
					S : 29.12	28.57
S-benzyliso-N-*p*-methoxyphenyl-TT	N-*p*-methoxy-phenylthiocarbamoyl-T	79	187	$C_{10}H_{12}N_2S_2O$	C : 49.58	50.00
					H : 4.85	5.08
					S : 27.58	26.66

TT—denotes thiocarbamoyl-thioacetamide,
T—denotes thioacetamide,
Characteristic IR frequencies (cm^{-1}) of N-phenylthiocarbamoyl-thioacetamide : 3220m, NH stretching (Lit[16] 3400-3100), 1170m, N – C(=S) – N grouping (Lit[16] 1200-1600), 1370, C=S grouping (Lit[17] 1400-1100).

follows :

To a paste of S-benzyliso-N-phenylthiocarbamoyl-thioacetamide (5 g) in chloroform (2 ml), was added bromine (1 ml) in small portions with vigorous stirring. Debenzylation was evident from the evolution of the lachrymatory fumes of benzyl bromide. After allowing the reaction mixture to stand for 30 minutes, it was washed with ether. Treatment of the residue with ethanol afforded the desired 3-phenylimino-5-methyl-1, 2, 4-dithiazole hydrobromide, which on basification with ammonia resulted in the free base (IV), which was crystallised from ethanol, m.p. 158°, (yield 65%). These results are presented in Table 2.

(iii) Oxidation of N-Arylthiocarbamoyl-thioacetamides(V) with bromine in dilute ethanol : The substituted-thioacetamides (5 g) (V) listed in Table 4 were oxidised with bromine (0.7 ml) in dilute ethanol solution. On addition of ether, the hydrobromides of the respective 1,2,4-dithiazoles(IV) got precipitated. Free bases were obtained by treating these with ammonia which were then crystallised from ethanol. These were found to be identical with the respective 3-arylimino-5-methyl-1,2,4-dithiazoles recorded in Table 2. The identity was confirmed from undepressed mixture melting points and superimposable IR spectra.

The results are given in Table 3.

N-Arylthiocarbamoyl-thioacetamides(V) :

(a) *Reductive debenzylation of S-benzyliso-N-arylthiocarbamoyl-thioacetamides(III) :* The appropriate S-benzyliso-N-arylthiocarbamoyl-thioacetamide (III) was dissolved in a mixture of pyridine and triethylamine (1 : 6) and a stream of dry hydrogen sulphide passed for 3 hrs. The reaction mixture on pouring over crushed ice and acidification with hydrochloric acid afforded the related N-arylthiocarbamoyl-thioacetamide(V), which was filtered out and crystallised from ethanol. The results are recorded in Table 4.

(b) *Reduction of 3-arylimino-5-methyl-1,2,4-dithiazoles(IV) with hydrogen sulphide in pyridine-triethylamine medium :* The related 1,2,4-dithiazoles(IV) were reduced in pyridine-triethylamine medium by passing dry hydrogen sulphide gas for about 2 hrs. On dilution with water and acidification of the resulting solution, the expected N-arylthiocarbamoyl-thioacetamide(V) was obtained. These were crystallised from ethanol.

Acknowledgement

Thanks are due to the Professor-in-charge, Applied Chemistry Section, Institute of Technology and the Head, Department of Chemistry, Banaras Hindu University for the facilities and one of us (R.R.) also expresses his gratitude to the University Grants Commission for a Junior Research Fellowship.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1170-1171

Synthesis and Insecticidal Activity of N⁴-Aryl-N¹-(O,O-dialkyl thiophosphoryl)Piperazines

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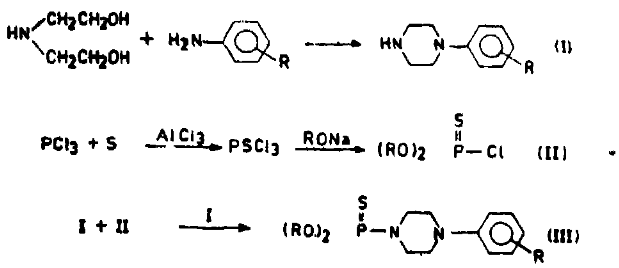
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Manuscript received 25 March 1980, accepted 26 July 1980

Eleven new N^4-aryl-N^1-(O,O-dialkyl thiophosphoryl) piperazines have been synthesised as possible insecticides by the condensation of N-aryl piperazines with O,O-dialkyl chloro-thiophosphates and tested against Periplanata americana.

VARIOUS disubstituted piperazines have been shown to possess broad spectrum pharmacological properties including antihistaminic[1], anthelmintic[2,3], antiemetic[4], antibacterial[5], acaricidal[6] and anticonvulsant[7] activities. Furthermore, anticonvulsants are known to exhibit acetylcholinesterase inhibition[8]. Organophosphates exhibiting potent antiacetylcholinesterase activity have been used extensively as important insecticides[9,10]. These observations encouraged us to synthesise the title compounds with the idea that the combined effect of the piperazine nucleus and O,O-dialkyl chlorothiophosphate might confer much enhanced insecticidal activity on these compounds.

In all eleven N^4-aryl-N^1-(O,O-dialkyl thiophosphoryl) piperazines(III) have been prepared according to the tentative scheme given below.



N-aryl piperazines(I) obtained according to known procedures[11], are listed in Table 1.

TABLE 1

Sl. No.	I R	Yield %	b.p.°C/mm	Lit. b.p.°C/mm
1.	2-CH_3	25	160-1/10	156-7/10
2.	3-CH_3	25	188-40/10	186.5-87.5/10
3.	4-CH_3	25	152-3/10	151-2.5/10
4.	4-Cl	40	110/2/2.5	156-7/5
5.	3-CF_3	85	Oil	m.p. 250-3 as HBr

Thiophosphorylchloride was prepared after the method of Gallar[12].

O,O-Dialkyl chlorothiophosphates(II) were prepared according to the method of Fletcher *et al*[13] (Table 2).

TABLE 2

Sl. No.	II R	Yield %	b.p.°C/mm	Lit. b.p.°C/mm
1.	Ethyl	50	74/7	96-99/25
2.	n-Butyl	53	153/5	95-8/0.7

N^4-Aryl-N^1-(O,O-dialkyl thiophosphoryl) piperazines(III) :

A solution of N-aryl piperazine (0.02 mole) in benzene (30 ml) was added dropwise to a solution of O,O-dialkylchlorothiophosphate (0.01 mole) in benzene (20 ml) under constant stirring. After complete addition of N-aryl piperazine additional benzene (20 ml) was added and the reaction mixture was stirred for further four hours. Then it was cooled and kept overnight. The separated solid, N-aryl piperazine hydrochloride, was filtered off and benzene from the filtrate was removed by distillation under reduced pressure. The crude product thus obtained was distilled in vacuum. The compounds thus prepared are listed in Table 3.

TABLE 3—N^4-ARYL-N^1-(O,O-DIALKYL THIOPHOSPHORYL)PIPERAZINES

Sl. No.	III R	III R_1	b.p.°C/mm	Mean K.D. time (hr) 0.5%	Mean K.D. time (hr) 0.1%
1.	C_2H_5	H	182-5/1.2	8.5	10.0
2.	C_2H_5	4-Cl	175-80/1	8.5	10.5
3.	C_2H_5	2-CH_3	170-3/1	7.5	10.5
4.	C_2H_5	3-CH_3	144-6/1	8.0	10.5
5.	C_2H_5	4-CH_3	160-3/1.5	8.0	9.5
6.	C_2H_5	3-CF_3	100-4/1.5	7.0	9.5
7.	n-C_4H_9	H	182-4/1.5	9.5	12.0
8.	n-C_4H_9	4-Cl	160-4/1	9.5	11.0
9.	n-C_4H_9	2-CH_3	152-4/1	—	—
10.	n-C_4H_9	4-CH_3	140-3/1.5	10.0	11.5
11.	n-C_4H_9	3-CF_3	117-20/1.5	10.0	12.5
				4.0	5.5(Control)
				40.0	40.0 Acetone

Nitrogen analysis the compounds is consistent with the respective composition.

Insecticidal Activity :

In the present study topical method of application by micrometer syringe was employed to test the toxicity of the compounds on adult cockroaches[14].

Acetone solutions of the compounds were applied at a dosage of 0.02 ml of 0.5% and 0.1% concentrations. The chemicals were injected between the 4th and 5th abdominal segments on the ventral side and treated insects were kept under observation for 24 hrs. During this period no food was given. For each sample ten replications were performed and insecticidal activity was determined as an average value. Parathion, a standard insecticide was used for control.

All the tested compounds have been found active against cockroaches (Table 3). From the insecticidal data it is observed that compounds nos. 1-6 (R = Ethyl) are more active than the compound nos. 7-11 (R = Butyl).

Acknowledgement

The authors wish to express their thanks to Head, Chemistry Department, Lucknow University, Lucknow for providing departmental facilities and to Dr. Nitya Nand, Director, C.D.R.I., Lucknow for microanalysis. One of them (OPB) is grateful to the CSIR, New Delhi, for financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1172-1173

Synthesis of N-Isonicotinyl-3-Methyl-4-(Substituted Hydrazono)-2-Pyrazolin-5-One

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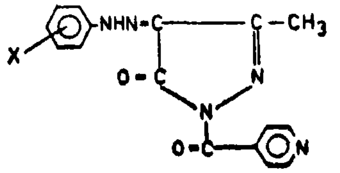
Manuscript received 7 May 1979, revised 17 April 1980, accepted 7 August 1980

Isonicotinic acid hydrazide (INH) and their derivatives are generally used as antitubercular and antitumor agent. We synthesised N^1-isonicotinyl-3-methyl-4-(substituted hydrazono)-2-pyrazolin-5-one and their derivatives.

THE chemistry[1] and wide range of pharmaceutical properties of 2-pyrazolin-5-one derivatives like germicides[2], antimicrobial agents[3], antiactincs[4], antidiurectics[5], analgesics and antipyretics[6], antifungals[7], antihistaminics[8], anti M.tuberculosis[9], antirheumatics[10], antibacterial[11] and similar such diseases have been cited in literature. Sulpha drugs are well known chemotherapeutic agents. Isonicotinic acid[12], isonicotinic acid hydrazide[13] and their derivatives are generally used as antitubercular and antitumor agents.

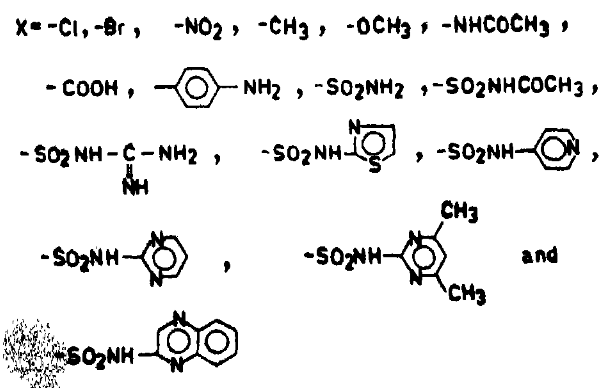
The method of preparation of 2-pyrazolin-5-one was first reported by Knorr[14]. Since then many new methods of synthesising the substituted 2-pyrazolin-5-one and their derivatives have been developed[15].

The present paper reports the reactions of diazotised sulpha drugs and aromatic amines at reactive methylene sites of β-ketoesters forming sulphasubstituted, phenyl hydrazono ethyl-2,3-dioxobutyrate[16]. The condensed product on cyclisation with INH gives N-isonicotinyl-3-methyl-4-(substituted hydrazono)-2-pyrazolin-5-one.



N^1-isonicotinyl-3-methyl-4-(X)-hydrazono-2-pyrazolin-5-one :

where



Experimental

IR spectra were recorded on Perkin-Elmer 621 Grading IR spectrophotometer. Solution spectra were measured in nujol mulls and KBr disc. The compounds were analysed for nitrogen on Coleman analyser and data were found well in agreement, within limits of the possible experimental error, with calculated values. The homogeneity and purity of the compounds were tested through TLC.

Synthesis of N-isonicotinyl-3-methyl-4-(X) hydrazono-2-pyrazolin-5-one :

Isonicotinic acid hydrazide (0.005 mole) and substituted phenyl hydrazono-ethyl-2, 3-dioxobutyrate (0.005 mole) were dissolved in sufficient quantity of glacial acetic acid and contents were refluxed on a water bath for three hours. On cooling, a solid coloured compound separated out. Filtered, dried and recrystallised from glacial acetic acid/DMF.

By adopting similar procedure, a few substituted-2-pyrazolin-5-ones have been synthesised and their characteristics are recorded in Table 1.

TABLE 1—CHARACTERISTICS OF N-ISONICOTINYL-3-METHYL-4-(X)-HYDRAZONO-2-PYRAZOLIN-5-ONE

Sl. No.	X	m.p.°C	Colour
1.	2.	3.	4.
1.	3-Chlorophenyl	185	DY
2.	4-Chlorophenyl	212	PY
3.	2-Methoxyl phenyl	227	O
4.	3-Methoxyl phenyl	155	RB
5.	4-Methoxyl phenyl	197	SDO
6.	2-Methyl phenyl	220	SDOF
7.	4-Methyl phenyl	192	SON
8.	3-Nitro, 4-methyl phenyl	225	DY
9.	4-Amino diaryl	248	SLBN
10.	2-Chloro, 4-nitrophenyl	233(d)	PY
11.	2,4,6-Tribromophenyl	202	BY
12.	N-Aceto-4-aminophenyl	230	B
13.	1-Naphthyl	257	SLBN
14.	2-Naphthyl	245	SDBN
15.	2-Sulphanilamido benzene	248	SOF
16.	N^1-2-Pyridyl sulphanilamido-benzene	245	DY
17.	N^1-2-Thiazolyl sulphanilamido-benzene	243	LO
18.	N^1-2-Pyrimidyl sulphanilamido-benzene	249	DY
19.	N^1-2-Guanyl sulphanilamido-benzene	250	DeY

(Table 1 Contd.)

20.	N^1-2-Acetyl sulphanilamido-benzene	230	PY
21.	N^1-2-(4,6-dimethyl)-pyrim'dyl sulphanilamido-benzene	255	DY
22.	N^1-2-Quinoxalyl sulphanilamido-benzene	172	B
23.	2,3-Dimethyl-1-phenyl-pyrazolone	210	SPeN
24.	4-Carboxyl phenyl	245	PY

(i) Elemental analysis of the compounds were found satisfactory.

(ii) Yield of the compounds ranged between 70 to 85%.

(iii) D=dark, De=dull, P=pale, Y=yellow, Pe=pink, S=shining, N=needles, B=brown, F=flakes, R=red, O=orange, L=light and (d)=decomposed.

IR Spectra :

The spectra had characteristic peaks 780 cm^{-1} (aromatic ring), 1520 cm^{-1} ($>C=C-NH-N=$), 1741 cm^{-1} ($>C=O$) amide, 1672 cm^{-1} ($>C=O$) cyclic, 1613 cm^{-1} ($>C=N$), 1560 cm^{-1} (heterocyclic five membered 2-pyrazolin-5-one ring) and 1480 cm^{-1} (six membered heterocyclic pyridine ring) were recorded which helps in establishing the structure of the compounds.

NMR Spectra :

The structure of 2-pyrazolin-5-ones were also confirmed by NMR spectra studies.

2-Pyrazolin-5-one :

NMR ($CDCl_3$) δ 2.48 (s, 3H, CH_3), 7.07-7.84 [(m, 8H, aromatic (two)] and 8.13-8.24 (s, 1H, $-NH$).

Acknowledgement

The authors wish to express their sincere thanks to Prof. M. K. Jain, Principal, Sahu Jain College, Najibabad for providing laboratory facilities and Dr. Shyam Singh, CDRI, Lucknow for recording I. R., NMR and chemical analysis.

The authors also wish to express their gratefulness to C.S.I.R., New Delhi for the award of S.R.F. to one of them (CPS).

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1174-1175

Synthesis of Organotin Thiophenols and Evaluation of Their Antifungal and Antibacterial Properties

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Manuscript received 29 January 1977, revised 2 January 1979, accepted 19 November 1979

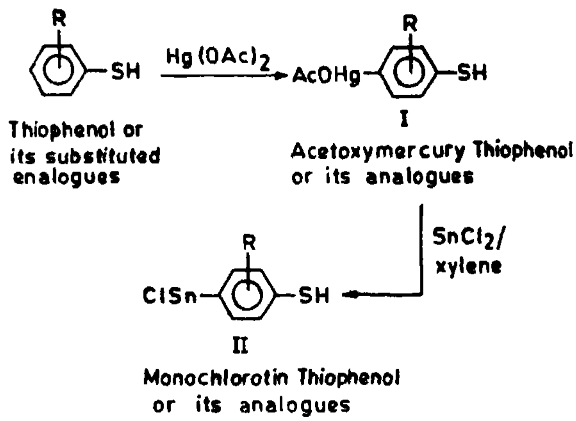
Thiophenol and its substituted analogues containing $-CH_3$, $-NH_2$ groups were used for the synthesis of their organotin derivatives through stannation of mercurials using anhydrous stannous chloride in xylene. Their fungicidal and bactericidal properties were studied and found to be quite encouraging.

IN these days of intensive agricultural practices, pesticides are invaluable in the promotion of farm productivity and protection of agricultural products during storage, besides their use in the control of certain vector-borne diseases such as malaria, typhus, yellow fever etc. Among the various synthetic pesticides, mercurated phenols are found to contain bactericidal properties as reported by Guhasircar and Rout[1,2].

Similarly Mehrotra and Dey[3] have reported pesticides like organotin phenols which are very suitable as the multi-protecting reagents against important fungi and bacteria of cereal crops. Observing the promise of organomercurial and organotin phenols as good pesticides, a few organomercurial and organotin thiophenols have been synthesised and their pesticidal properties (both antifungal and antibacterial) have been evaluated.

Experimental

Thiophenol was mercurated with equimolecular quantities of mercuric acetate in presence of glacial acetic acid and ethyl alcohol[4]. The resultant acetoxymercury thiophenol was converted into its corresponding monochlorotin phenol by refluxing it in dry xylene on an oil bath for 14 hrs with an equimolecular amount of anhydrous stannous



chloride. The tin compound thus formed was then isolated by removing xylene and was then recrystallised in acetone (II, 75%), m.p. 175°. Found: Sn^4, 45.3%. C_6H_5 SnCl requires Sn 45.08%. Their bactericidal behaviours were studied using potato-dextrose agar media. The fungi selected for these studies included *Aspergillus niger* and *Chetomium globossum* and bacteria covering *Staphylococcus aureus* and *Escherichia coli.* The analytical data and the pesticidal properties are given in Table 1.

The structure of the compounds were confirmed on the basis of the position of acetoxymercury group

TABLE 1—NAME OF TIN COMPOUNDS AND THEIR PESTICIDAL PROPERTIES

Sl. No.	Nature of R	m.p.°C	Yield	Colour	Tin Percentage		Pesticidal Properties			
					Found	Calcd	Antifungal		Antibacterial	
							A.N.	*C.G.*	*E.C.*	*S.A.*
1.	H−	175	75%	A	45.3	45.08	+	++	+	++
2.	2-CH_3	189	60%	Y.W.	43	42.6	+	+	+	+
3.	4-CH_3	195	40%	Y.W.	42.9	42.6	+	+	+	+
4.	2-NH_2	210	45%	G.W.	42.7	42.5	++	++	++	++

− Stands negative mortality.
\+ Stands mortality upto 50%.
++ Stands mortality more than 50%.
A = Ash.
G = Grey.
Y.W. = Yellowish White.
G.W. = Greyish White.

in the mercurated compounds established earlier by Rohatgi[5].

Acknowledgement

The author is grateful to the Head of the Department of Chemistry, S.C.S. College, Puri and Head of the Department of Botany, C.R.R.I., Cuttack for providing facilities for work. My special thanks are due to Dr. A. K. Panigrahi for his valuable suggestions.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1176-1180

Fluorine Containing Bioactive Heterocycles : Part I. Synthesis and Antibacterial, Fungicidal and Antiviral Activities of Some New Fluorine Containing 3-Dialkylamino-ethylthio-5-Morpholinomethyl[1,2,4]Triazino[5,6-b]Indoles and 3-[2-(5-Benzylidene-4-Thiazolidinone)Diazo]Indol-2-Ones

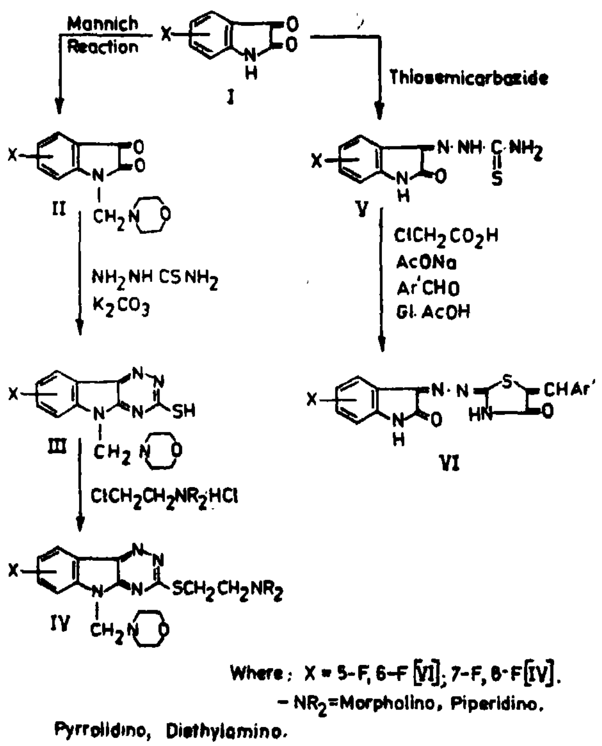
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Manuscript received 18 November 1979, revised 22 July 1980, accepted 29 October 1980

A series of new fluorine containing 3-dialkyl-aminoethylthio-5-morpholinomethyl [1,2,4]triazino[5,6-b]indoles and 3-[2-(5-benzylidene-4-thiazolidinone)diazo]indol-2-ones have been synthesized; the former by the reaction of different dialkylaminoethyl chloride hydrochloride with fluorinated 5-morpholinomethyl[1,2,4]triazino[5,6-b]indole-3-thiones in presence of sodium hydroxide and the latter, by treating fluorinated isatin-3-thiosemicarbazones, chloroacetic acid and sodium acetate with different aryl aldehydes in glacial acetic acid. All the synthesized compounds have been characterized by their spectral and elemental analysis. All the compounds have been screened for their antibacterial activity against gram positive bacteria *Staphylococcus albus* and gram negative bacteria *Escherichia coli*. A representative number of compounds have been screened for their antifungal activity against *Alternaria burnsii* and also for their antiviral activities.

THE indole nucleus is well known for its pharmaceutical and biochemical activities[1,2]. Indole-2,3-dione, an important indole derivative, is found to possess antiviral[3], antifungal[4] and antibacterial[5] activity. 5-Bromoisatin has shown analgesic activity stronger than that of aspirin[6]. Various triazino[5,6-b]indoles have been synthesized and most of them have shown antiviral and antibacterial activities[7]. Isatin-β-thiosemicarbazones are well known antiviral agents against rabbitpox, cowpox, alastrin and various viruses[8,9]. Indolylthiazolidinones have also been found to possess antiviral and antimicrobial activities[10,11]. These observations prompted us to undertake the synthesis of fluorine containing 3-dialkylaminoethylthio-5-morpholinomethyl[1,2,4]-triazino[5,6-b]indoles and 3-[2-(5-benzylidene-4-thiazolidinone)diazo]indol-2-ones [Scheme-I].



Where: X = 5-F, 6-F [VI]; 7-F, 8-F[IV].
– NR_2=Morpholino, Piperidino, Pyrrolidino, Diethylamino.
– Ar' = 4-Fluorophenyl, Phenyl, 4-Chlorophenyl, 2-Furyl, 4-Nitrophenyl, Dimethylaminophenyl.

SCHEME-I

Experimental

Melting points of all synthesized compounds are uncorrected. Infrared spectra were recorded on Perkin-Elmer (model-337) in KBr Pellets. PMR spectra were recorded in trifluoroacetic acid (TFA) on Perkin-Elmer (model-RB-12; 60 MHz). TMS was takan as an internal standard.

5/6-Fluoroindole-2,3-diones(I) :

These compounds were synthesized according to the method of Yen[12] and Sadler[13] from 4-fluoroaniline and 3-fluoroaniline respectively. 5-Fluoroindole-2,3-dione, yield 62%, m.p. 221-2° (Lit.[12] m.p.

223°) ; 6-Fluoroindole-2,3-dione, yield 64%, m.p. 195-6° (Lit.[13] m.p. 197°).

5/6-Fluoro-1-morpholinomethylindole-2,3-diones(II) :

The compounds were synthesized according to the method of Wyeth[14]. A mixture of required 5/6-fluoroindole-2,3-dione (0.01 *M*), morpholine (0.012 *M*) and formaldehyde (0.015 *M*) in ethanol (20 ml) was refluxed for 40 minutes. On cooling the reaction mixture, crystals separated out which were recrystallized from ethanol. 5-Fluoro-1-morpholinomethyl-indole-2,3-dione, yield 73%, m.p. 150° (Found : N 10.51 calculated for $C_{13}H_{13}FN_2O_3$,N, 10.60%) ; 6-Fluoro-1-morpholinomethylindole-2,3-dione, yield 68%, m.p. 155° (Found : N 10.42 calculated for $C_{13}H_{13}FN_2O_3$, N, 10.60%).

7/8-Fluoro-5-morpholinomethyl-[1,2,4]-triazino[5,6-b] indole-3-thiones(III) :

A mixture of appropriate 1-morpholinomethyl-indole-2,3-dione (0.01 *M*) and thiosemicarbazide (0.011 *M*) was refluxed with potassium carbonate (0.015 *M*) in water for 5-6 hours[15]. The solution was filtered, cooled and acidified to give corresponding 5-morpholinomethyl[1,2,4]triazino[5,6-b] indole-3-thione, which was purified by recrystallization from DMF and gave single spot in TLC in various solvent systems.

7-Fluoro-5-morpholinomethyl-[1,2,4]triazino[5,6-b] indole-3-thione, yield 61% m.p. >300° (Found : N 21.78 calculated for $C_{14}H_{14}N_5FOS$, N, 21.94%) ; 8-Fluoro-5-morpholinomethyl[1,2,4]triazino[5,6-b] indole-3-thione, yield 64%, m.p. >300° (Found : N 21.71 calculated for $C_{14}H_{14}N_5FOS$, N, 21.94%).

3-Dialkylaminoethylthio-7/8-fluoro-5-morpholinomethyl[1,2,4]triazino[5,6-b]indoles(IV) :

These derivatives were synthesized according to the method of Gladych *et al*[16]. The aqueous solution of dialkylaminoethylchloride hydrochloride (0.015 *M*) was added to a stirred mixture of appropriate fluorinated 5-morpholinomethyl-[1,2,4] triazino [5,6-b] indole-3-thione (0.01 *M*) in *N* sodium hydroxide (10 ml). The mixture was diluted, acidified, filtered and the filtrate was made alkaline to give the desired compound. All synthesized compounds gave single spots in T. L. C. Their analytical data and antibacterial activity are given in Table 1.

5/6-Fluoroisatin-3-thiosemicarbazones(V) :

A mixture of 5/6-fluoroindole-2,3-dione (0.01 *M*) and thiosemicarbazide (0.01 *M*) in ethanol (25 ml) was refluxed for 40 minutes. On cooling the reaction mixture, crystals separated out which were filtered and recrystallized from ethanol.

5-Fluoroisatin-3-thiosemicarbazone, yield 94%, m.p. 275-6° ; 6-Fluoroisatin-3-thiosemicarbazone, yield 97%, m.p. 240-1°.

3-[2-(5-Benzylidene-4-thiazolidinone) diazo]-5/6-fluoroindol-2-ones(VI) :

A mixture of 5/6-fluoroisatin-3-thiosemicarbazide (0.01 mole), chloroacetic acid (0.015 mole) and sodium acetate (0.01 mole) was refluxed in glacial acetic acid (20-30 ml) for half an hour. An appropriate aryl aldehydes (0.01 mole) was then added and the mixture further refluxed for 4-5 hours[10], cooled and filtered. Analytical data and antibacterial activity of compounds prepared are given in Table 2.

Evaluation of biological activity :

The antibacterial activity of all synthesized compounds was studied[17] against gram positive bacteria *Staphylococcus albus* and gram negative bacteria *Escherichia coli* in different concentrations ranging from 4 μg/ml-20 μg/ml. Antibacterial activity at two particular concentrations, 16 μg/ml and 20 μg/ml, is being given in Tables 1 and 2.

The fungicidal activity of compounds of type VI was studied against *Alternaria burnsii* according to method[18]. The test fungus was grown on Potato Dextrose Agar medium, in which desired amount of fungicide was previously incorporated in 500 ppm and 1000 ppm concentration ; control consisted of plane PDA plates inoculated with pathogen. The linear growth at 25° was measured after 7 days.

The antiviral activity of some of the compounds (Nos. 1, 8 of Table 1 and Nos. 1, 8 of Table 2) was studied against *Semliki forest* virus. 2 mg quantity of each of the compounds was given to test mouse (20 gram) in two divided doses (1 mg each injection) at 24 and 48 hours after virus challenge (100 LD 50).

Results and Discussion

Spectral Studies (IR & PMR) :

Indole-2,3-diones I, show strong absorption bands in the region of 3300-3500 cm^{-1} (>N–H stretching) and strong >C=O absorption in the range of 1735-1730 cm^{-1}. When compounds I were subjected to Mannich reaction, yielding compounds II, new resonance signals appeared due to –N.CH_2–N– protons at δ 4.35 ppm. Further, >NH absorption band disappeared providing a strong support for formation of N-Mannich bases. Compounds II when treated with thiosemicarbazide and potassium carbonate gave III, and the structure of latter confirmed by disappearances of >CO absorption bands (1735-1730 cm^{-1}) and appearance of new –C=N absorption band between 1630-1600 cm^{-1}. Compounds III, on treatment with

Table 1—Analytical Data and Antibacterial Activity of Fluorine Containing 3-Dialkylaminoethylthio-5-morpholinomethyl[1,2,4]triazino[5,6-b]indoles IV :

Sl. No.	X Substituent in Ar	$-NR_2$	m.p. °C	Yield %	Molecular formula	N% analysis Calcd.	N% analysis Found	Antibacterial activity S. albus 16 µg/ml	S. albus 20 µg/ml	E. coli 16 µg/ml	E. coli 20 µg/ml
1.	8-F	Diethylamino-	286	71	$C_{20}H_{27}N_6FOS$	20.09	19.85	++	++	+	++
2.	8-F	Piperidino-	212	62	$C_{21}H_{27}N_6FOS$	19.53	20.22	+	++	+	++
3.	8-F	Pyrrolidino-	201	71	$C_{20}H_{25}N_6FOS$	20.19	20.01	±	±	+	+
4.	8-F	morpholino-	221	66	$C_{20}H_{25}N_6FO_2S$	19.44	19.60	±	±	+	++
5.	7-F	Diethylamino-	228	69	$C_{20}H_{27}N_6FOS$	20.09	20.25	+	++	++	+++
6.	7-F	Piperidino-	232	65	$C_{21}H_{27}N_6FOS$	19.53	19.15	+	++	+	++
7.	7-F	Pyrrolidino-	>300	70	$C_{20}H_{25}N_6FOS$	20.19	20.30	±	±	±	+
8.	7-F	morpholino-	229	68	$C_{20}H_{25}N_6FO_2S$	19.44	19.41	+	+	+	+

– Insensitive.
± 0.1 to 0.3 cm area of inhibition of bacterial zone.
+ 0.3 to 0.5 cm ,, ,, ,, ,,
++ 0.5 to 0.7 cm ,, ,, ,, ,,
+++ 0.7 to 0.9 cm ,, ,, ,, ,,

Table 2—Analytical Data and Antibacterial Activity of Fluorine Containing 3-[2-(5-Benzylidene-4-Thiazolidinone)diazo]-Indol-2-ones VI :

Sl. No.	X Substituent in Ar	Ar′	m.p. °C	Yield %	Molecular formula	N% analysis Calcd.	N% analysis Found	Antibacterial activity S. albus 16 µg/ml	S. albus 20 µg/ml	E. coli 16 µg/ml	E. coli 20 µg/ml
1.	6-F	Phenyl	272-4	69	$C_{18}H_{11}N_4FO_2S$	15.30	15.12	±	±	+	+
2.	5-F	Phenyl	>300	67	$C_{18}H_{11}N_4FO_2S$	15.30	15.21	±	±	±	+
3.	6-F	4-F Phenyl-	>300	95	$C_{18}H_{10}N_4F_2O_2S$	14.58	14.39	+	++	++	+++
4.	5-F	4-F Phenyl-	247 (decomp.)	85	$C_{18}H_{10}N_4F_2O_2S$	14.58	14.41	+	++	++	++
5.	5-F	Dimethylaminophenyl-	255	81	$C_{20}H_{16}N_5FO_2S$	17.11	17.01	±	±	±	+
6.	6-F	Dimethylaminophenyl-	242	78	$C_{20}H_{16}N_5FO_2S$	17.11	16.98	±	±	+	++
7.	5-F	4-Cl Phenyl-	>300	77	$C_{18}H_{10}N_4O_2FClS$	13.98	13.89	+	+	+	++
8.	6-F	4-Cl Phenyl-	>300	91	$C_{18}H_{10}N_4O_2FSCl$	13.98	13.82	±	±	+	++
9.	5-F	2-furyl-	276	82	$C_{15}H_9N_4FO_3S$	15.73	15.68	±	±	+	+
10.	6-F	2-furyl-	>300	83	$C_{16}H_9N_4FO_3S$	15.73	15.52	±	±	+	+
11.	5-F	4-NO_2 phenyl-	>300	87	$C_{18}H_{10}N_5FO_4S$	17.03	17.00	++	+++	+++	+++
12.	6-F	4-NO_2 phenyl-	325-6	90	$C_{18}H_{10}N_5FO_4S$	17.03	16.98	++	+++	++	+++

– Insensitive.
± 0.1 to 0.3 cm area of inhibition of bacterial zone.
+ 0.3 to 0.5 cm ,, ,, ,, ,,
++ 0.5 to 0.7 cm ,, ,, ,, ,,
+++ 0.7 to 0.9 cm ,, ,, ,, ,,

dialkylaminoethylchloride hydrochloride gave IV, the PMR spectra of which show resonance signals between δ 3.5 to 4.2 ppm (broad due to $-SCH_2CH_2-N$ protons and $N-CH_2$ protons and aromatic protons signal in the range of δ 7.0-8.0 ppm. Compounds IV, show absorption bands at 1630-1600 cm^{-1} ($-C=N$ stretching).

Compounds I, on treatment with thiosemicarbazide gave V, which show three different >NH absorptions between 3500-3300 cm^{-1} and >C=O absorption bands in the range of 1735-1730 cm^{-1}. Compound V, when cyclized with chloroacetic acid, gave compounds VI which show broad absorption bands due to >NH stretching between 3500-3300 cm^{-1}.

In all the above compounds, the absorption bands due to Ar. C-F appears between 1260-1200 cm^{-1}.

Biological Activity :

The antibacterial activity of the compounds indicated that all compounds are effective against gram negative bacteria *Escherichia coli*. Compounds having $-NO_2$ group were found to be more powerful antibacterial agents as compared to other analogs (Table 2).

The fungicidal activity of 3-[2-(5-benzylidene-4-thiazolidinone)diazo]indol-2-ones has been given

TABLE 3—FUNGICIDAL ACTIVITY OF FLUORINE CONTAINING 3-[2-(5-BENZYLIDENE-4-THIAZOLIDINONE)DIAZO]-INDOL-2-ONES IV : [AGAINST "ALTERNARIA BURNSII"]

Sl.* No.	No. of replicates	Average growth of fungus (in m.m.) At 1000 ppm	At 500 ppm	Average % of inhibition At 1000 ppm	At 500 ppm
1.	3	18	15	40	50
2.	3	13	12	56	60
3.	3	8	10	73	66
4.	3	10	13	66	56
5.	3	5	10	83	66
6.	3	4	5	86	83
7.	3	2	4	93	86
8.	3	2	3	93	90
9.	3	13	10	56	66
10.	3	15	17	40	43
11.	3	1	5	96	83
12.	3	2	7	93	76
Control		30	30		

* The serial number of compounds correspond to those given in Table 2.

in Table 3. The percentage inhibition was calculated according to Vincent's (1947) formula which is as follows :

$$\% \text{ inhibition} = \frac{Ac - At}{Ac} \times 100$$

Ac = Area of the colony in control plate, At = Area of the colony in test plate.

The results indicated that compounds Nos. 7,8, 11,12 show greater inhibition at 1000 ppm. Compounds containing $-NO_2$ and $-Cl$ cause greater inhibition in the growth of fungus.

The antiviral activity of four compounds Nos. 1,8 (Table 1), Nos 1,8 (Table 2) have been tested. The protection rate (survival %) and MST (Mean survival time) was calculated by following formulae :

$$\% \ S = \frac{\text{Survival number of animals}}{\text{Initial number of animals}} \times 100$$

$$MST = \frac{\text{Summation of time taken for each animal to die + Summation of Survival time of animal not dying}}{\text{Number of animals dying + Number of animals surviving}}$$

The results indicated that only one compound 3-[2-(5-chlorobenzylidene)-4-thiazolidinone)diazo]-6-fluoroindol-2-one possess some activity.

Acknowledgement

The authors are very grateful to Dr. B. M. Gupta, Head, Division of Virology for permission to evaluate the antiviral activity at Central Drug Research Institute, Lucknow. We are also thankful to Prof. J. S. Mathur, Department of Pathology, S.M.S. Medical College, Jaipur for providing facilities for antibacterial activity. One of us (S. K. J.) is thankful to CSIR, New Delhi for providing financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1181-1184

Terpenoids and Related Compounds : Part 29[1]. Molecular Rearrangements of Glut-5α, 6α-epoxy-3β-yl Acetate

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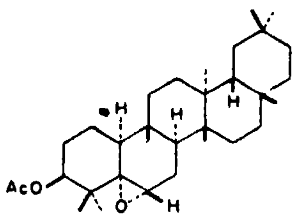
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Manuscript received 30 May 1980, accepted 9 September 1980

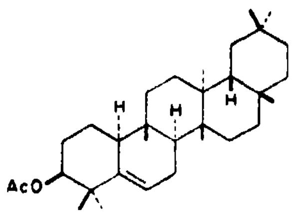
Molecular rearrangements of glut-5α, 6α-epoxy-3β-yl acetate (1) were studied with aqueous perchloric acid and with borontrifluoride etherate in benzene. While the former reagent furnished the diene (3) and the enediol (4a), the latter reagent yielded the diene (13) and the enediol monoacetate (14a).

IN a general programme for the study of molecular rearrangements of friedooleanane derivatives[1-6], we have undertaken a study on the action of aqueous perchloric acid and of borontrifluoride etherate on glut-5α, 6α-epoxy-3β-yl acetate(1), prepared by epoxidation of glut-5-en-3β-yl acetate(2) with *m*-chloroperbenzoic acid.

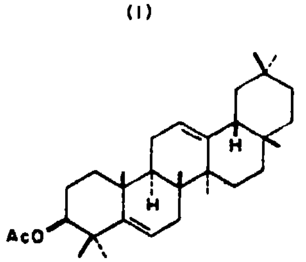
The mass spectra of the epoxide (1) revealed fragmentation patterns in agreement with those of similar class of triterpenoids[7-9]. The α-orientation of the epoxide oxygen was favoured from steric considerations and also from nmr spectra. The proton at C-6 appeared as a quartet (1H) around δ 3.1 ppm (J_{ee} = 3Hz and J_{ae} = 4Hz).



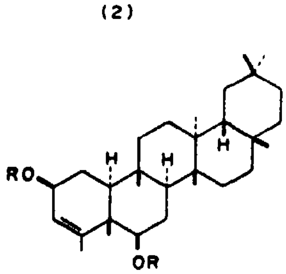
(1)



(2)



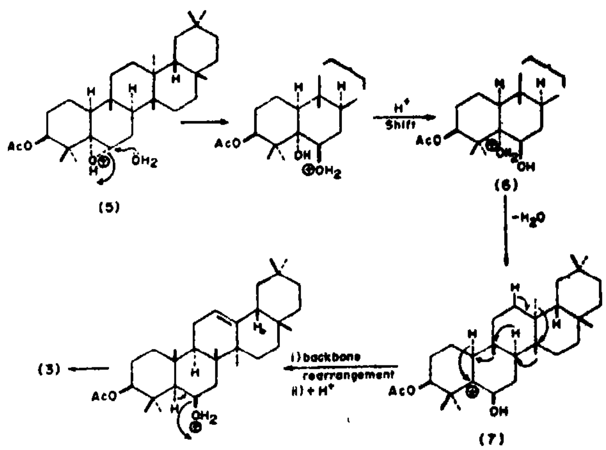
(3)



(4)

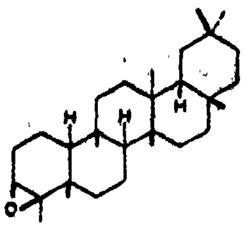
a, R = H
b, R = Ac

Treatment of the epoxide (1) with aqueous perchloric acid in tetrahydrofuran for 10 hr at room temperature gave two isolable products besides the unchanged starting material. The least polar product (ca 20%) was a nonconjugated diene, which was shown to be gluta-5, 12-dien-3β-yl acetate (3) from uv, ir, nmr and mass spectral data (see Experimental). The next polar product (ca 60%) was the unchanged epoxide (1). The most polar product (ca 10%) was shown to be a new diol (4a), which furnished a diacetate (4b). The structures of (4a) and (4b) were established from uv, ir, nmr and mass spectral data (see Experimental). The suggested mechanistic interpretation for the formation of (3) involving nucleophilic attack by water on the protonated epoxide (5) is shown in Scheme 1.

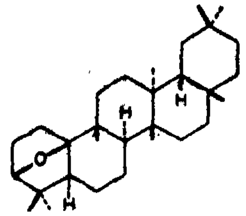


SCHEME I.

The departure of H_2O and the backbone rearrangement from the cation (6) was not a synchronous process because of the unfavourable configuration of the substitution at C-5. It may be visualised that the classical cation (7) was first formed which triggered the subsequent backbone rearrangement and final elimination of H_2O to produce the diene (3). A similar situation was encountered by Torii *et al*[10] in the rearrangement of D : A-friedooleana-3β, 4β-epoxide (8) to dendropanoxide(9).

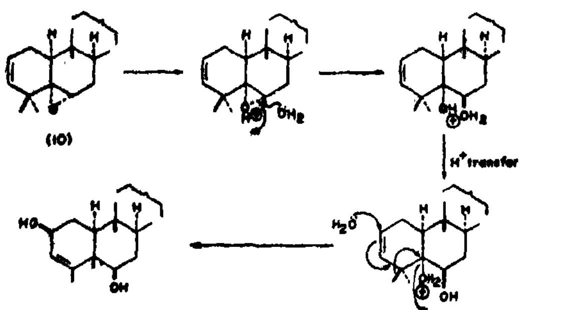


(8)



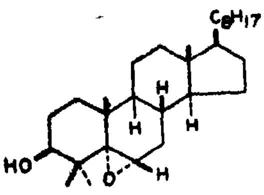
(9)

The formation of the diol (4a) in very small amount (ca 10%) could be explained in the following manner. The acetoxy group (or the hydroxyl group formed in small amount in presence of aqueous perchloric acid) at C-3 was β-axial and so could lead to the olefinic epoxide (10) in presence of acid. The subsequent steps are shown in Scheme 2.

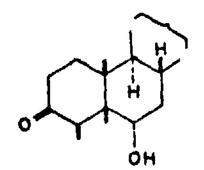


SCHEME 2

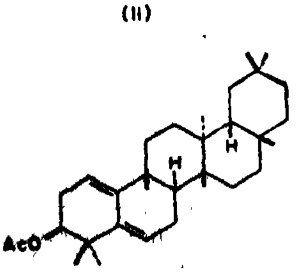
A similar migration of 4β-methyl group to 5β position had been reported earlier by Halsall *et al*[11] when the epoxide(11) was converted to the hydroxy ketone (12) on treatment with BF_3-ether complex.



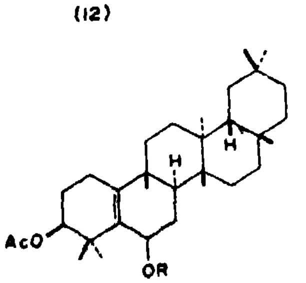
(11)



(12)

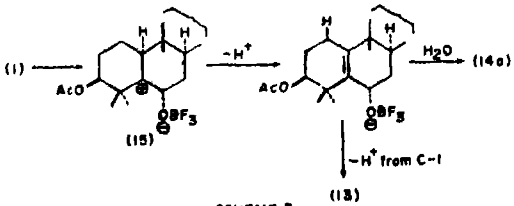


(13)



(14) a, R = H
b, R = Ac

Finally the epoxide (1) on treatment with BF_3-etherate in anhydrous benzene for 30 min at room temperature furnished a mixture which could be resolved by chromatography into two components. The less polar one (ca 30-40% yield) was identified as the previously known gluta-1 (10), 5-dien-3β-yl acetate (13)[12] while the more polar component was shown to be glut-5 (10)-en-3β-acetoxy-6α-ol (14a). The latter was converted into the diacetate (14b), whose structure was established on the basis of uv, ir, nmr and mass spectral data (see Experimental). In a nonpolar solvent like benzene the epoxide (1) formed the ion-pair (15) in a cage of solvent when treated with BF_3-ether complex. The subsequent steps leading to (13) and (14a) are shown in Scheme 3.



SCHEME 3.

Experimental

All m. ps were uncorrected. Pet ether used had b.p. 60-80°. The optical rotations were taken in chloroform solution.

Epoxidation of Glut-5-en-3β-yl acetate (2) :

m-Chloroperbenzoic acid (2.5 g) in chloroform (50 ml) was added with stirring to a solution of glut-5-en-3β-yl acetate (2, 2 g) in chloroform (50 ml) kept at 0°. The reaction was followed by t.l.c. on silica gel and was complete within 8 hr. Usual work up yielded a crystalline residue which on crystallisation from chloroform-acetone gave glut-5α, 6α-epoxy-3β-yl acetate (1), m.p. 216-218° C ; $[\alpha]_D$ = +47.6° (Found : C, 79.55 ; H, 10.48. $C_{32}H_{52}O_3$ requires : C, 79.28 ; H, 10.81%) ; ν_{max}^{nujol} 1730, 1260 (acetate), 1380, 1360 (gem dimethyl), 892, 800 (epoxy ring) cm^{-1} ; (nmr has been discussed earlier) ; m/e 484 (M^+, 100%), 424 ($[M-CH_3COOH]^+$, 24.38%), 469 ($[M-CH_3]^+$, 47.17%), 205 (54.04%), 135 (18.84%) and 119 (23.10%).

Reaction of the Epoxide (1) with Aqueous Perchloric Acid :

A suspension of the epoxide (1, 1.5 g) in tetrahydrofuran (60 ml) was treated dropwise with perchloric acid (3*N*, 11 ml) and the mixture was stirred for 10 hr at room temperature. Then 5% sodium hydrogen carbonate solution was added and the product was extracted with ether. The residue (1.5 g) from the ether extract on chromatography over a column of silica gel (100 g) furnished three

components. The first component from benzene-petroleum ether (1 : 9) was *gluta-5, 12-dien-3β-yl acetate* (3, 0.25 g), m.p. 208-210° (chloroform-methanol) ; $[\alpha]_D = +11.8°$ (Found : C, 82.28 ; H, 10.85. $C_{32}H_{50}O_2$ requires : C, 82.34 ; H, 10.80%) ; ν_{max}^{nujol} 1730, 1255 (acetate), 1380, 1360 (gem-dimethyl) and 840 (trisubstituted double bond) cm^{-1}. ^1H nmr, δ ($CDCl_3$) 1.95 (3H, S, $OCOCH_3$), 5.1 br (1H, 6-H), 5.55 br (1H, 12-H), 4.6 [1H, q, J = 10 Hz ($\phi_{aa} \cong 180°$) and J = 6 Hz ($\phi_{ae} \cong 60°$), 3-H], 0.8 – 1.05 (eight tertiary methyls) ; m/e 466 (M^+), 406 ($[M-CH_3COOH]^+$, 100%), 391 ($[M-\{CH_3COOH+CH_3\}]^+$, 12.84%), 259 (57.90%), 132 (46.03%), 205 (36.23%) and 171 (30.43%).

The second component (0.9 g) eluted from the column with benzene-petroleum ether (1 : 4) had m.p. 212-215° (chloroform-acetone) and was identical in all respects with the starting epoxide (1) (ir, Co-TLC, mixed m.p.).

The most polar component eluted with benzene-ethyl acetate (9 : 1), corresponded to *friedel-3-en-2β, 6β-diol* (4a, 0.25 g). Recrystallisation from chloroform-methanol gave the pure diol (4a), m.p. 280-285° ; $[\alpha]_D = +8°$, ν_{max}^{nujol} 3340 br (OH), 1375, 1360 (gem-dimethyl) and 840 cm^{-1} (trisubstituted double bond). ^1H nmr, δ ($CDCl_3$) 5.5 (1H, ill-defined multiplet, 3-H), 3.25 br (2H, 2×OH, disappeared on D_2O exchange), 3.45 (1H, m, 6-H), 4.25 (1H, m, allylic proton on C-2), 1.0-1.3 (seven tertiary methyls) ; m/e 442 (M^+), 424 ($[M-H_2O]^+$, 100%), 406 ($[M-\{H_2O+H_2O\}]^+$, 12.37%), 391 ($[M-\{2H_2O+CH_3\}]^+$, 14.34%), 205 (44.08%) and 135 (38.33%).

The diol (4a, 0.1 g) was acetylated as usual with Ac_2O (1 ml) and pyridine (1 ml) and the product on crystallisation from chloroform-methanol yielded *friedel-2β, 6β-diacetoxy-3-ene* (4b), m.p. 262-268° (Found : C, 77.43 ; H, 10.29. $C_{34}H_{54}O_4$ requires : C, 77.52 ; H, 10.33%) ; ν_{max}^{nujol} 1735, 1245 (acetate), 1375, 1360 (gem-dimethyl) and 840 (trisubstituted double bond) cm^{-1}. ^1H nmr, δ ($CDCl_3$) 1.9 and 1.95 (6H, S, 2×$OCOCH_3$), 5.3 (2H, m, methine proton on C-2 + olefinic proton on C-3 ; the chemical shift of the methine proton on C-2 is expected to fall in the olefinic region[18].), 4.6 [1H, q, J = 11 Hz ($\phi_{aa} \cong 180°$) and J = 7 Hz ($\phi_{ae} \cong 60°$), 6-H], 0.75-1.3 (seven tertiary methyls). The methyl group attached to the olefinic bond at C-4 appeared slightly in the downfield region δ 1.5 ppm due to the deshielding effect of the double bond.

Reaction of the Epoxide(1) with Borontrifluoride Etherate :

A solution of the epoxide (1, 1 g) in dry benzene (50 ml) was treated with freshly distilled borontrifluoride etherate (1 ml) and the mixture was stirred for 30 min at room temperature, when the mixture became pale yellow. Usual work up furnished a gummy mass (1.2 g) which was chromatographed over a column of silica gel (100 g). Benzene-petroleum ether (1 : 9) eluted *gluta-1(10), 5-dien-3β-yl acetate* (13, 0.35 g), m.p. 210-215° (chloroform-acetone) (lit.[18], 208-210°) ; $[\alpha]_D = +37.7°$ (Found : C, 82.09 ; H, 10.73. calc. for $C_{32}H_{50}O_2$: C, 82.34 ; H, 10.80%) ; $\lambda_{max}^{EtOH}(\epsilon)$ 232 (16 500), 238 (18 000) and 246 nm (inflection) (11 000) ; ν_{max}^{nujol} 1730, 1245 (acetate), 1380, 1365 (gem-dimethyl) and 860 (trisubstituted double bond) cm^{-1}. ^1H nmr, δ ($CDCl_3$) 1.95 (3H, S, $OCOCH_3$), 5.1 br (1H, 6-H), 5.55 br (1H, 1-H), 4.6 [1H, q, J = 10 Hz ($\phi_{aa} \cong 180°$) and J = 6 Hz ($\phi_{ae} \cong 60°$), 3-H], 0.8-1.05 (eight tertiary methyls) ; m/e 466 (M^+), 406 ($[M-CH_3COOH]^+$, 100%), 391 ($[M-\{CH_3COOH+CH_3\}]^+$, 27.46%), 253 (3.79%), 171 (39.22%) and 205 (58.05%).

Subsequent elution of the column with benzene yielded *glut-5(10)-en-3β-acetoxy-6α-ol* (14a) (0.6 g), m.p. 232-235° (chloroform-methanol) ; $[\alpha]_D = +129.6°$; ν_{max}^{nujol} 3400 br (OH), 1740 and 1245 (acetate) cm^{-1}. The hydroxy compound (14a) was acetylated with a mixture of acetic anhydride and pyridine in the usual manner to furnish the diacetate (14b), m.p. 155-160° (chloroform-methanol) ; $[\alpha]_D = +158.3°$ (Found : C, 77.08 ; H, 10.49. $C_{34}H_{54}O_4$ requires : C, 77.52 ; H, 10.33%) ; ν_{max}^{nujol} 1735, 1250 (acetate), 1380 and 1365 (gem-dimethyl) cm^{-1}. ^1H nmr, δ ($CDCl_3$) 1.9 and 2.0 (6H, S, 2×$OCOCH_3$), 5.2 br (2H, m, α-H on C-3 + β-H on C-6), 0.8-1.1 (eight tertiary methyls). Absence of any olefinic proton indicated the tetrasubstituted nature of the double bond. m/e 526(M^+), 466 ($[M-CH_3COOH]^+$, 100%), 406 ($[M-\{CH_3COOH+CH_3COOH\}]^+$, 43.48%), 391 ($[M-\{2\times CH_3COOH+CH_3\}]^+$, 34.45%), 205 (51.15%), 253 (4.48%), 171 (31.86) and 135 (12.86%).

Acknowledgement

We thank Dr. A. Wegmann, Department of Chemistry, Stanford University, U.S.A. for the mass spectral data. We are grateful to the Council of Scientific and Industrial Research, New Delhi, India for the award of a Junior Research Fellowship to S.N.M.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1185-1190

Kinetics of Oxidation of α-Aminoacids by Sodium N-Chloro-4 Methyl Benzene Sulphonamide in Perchloric Acid Medium

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Manuscript received 20 February 1979, revised 13 March 1980, accepted 31 March 1980

A kinetic study of oxidation of leucine, serine, glutamine and glutamic acid by Sodium-N-Chloro-4 methyl benzene sulphonamide or Chloramine-T (CAT) in presence of $HClO_4$ has been made at 30°. The reaction shows first order dependence each on CAT and amino acid and is inverse first order with respect to H^+ ion. Ionic strength and presence of the added reaction product, *p*-toluenesulphonamide have no effect on the rate. Chloride ion catalyses the reaction. The reaction was studied at different temperatures and the activation parameters have been evaluated. A mechanism in which the zwitterion interacts with protonated CAT has been proposed to account for the observed kinetics.

SODIUM-N-chloro-4 methyl benzene sulphonamide or Chloramine-T (p-CH_3-$C_6H_4SO_2NCl\,Na.3H_2O$) behaves as an oxidising agent both in acid and alkaline media[1]. This organic compound containing positive halogen undergoes a two electron change in its reactions. The oxidation potential of chloramine-T/sulphonamide system is *p*H dependent and decreases with increase in *p*H of the medium[2]. Chloramine-T (CAT) is of special interest for studying reaction mechanisms as it behaves both as chlorinating and oxidising agent. It furnishes different types of reactive species in solution, such as monochloramine-T, (RNHCl where $R = p$-$CH_3C_6H_4SO_2$), dichloramine-T ($RNCl_2$) and HOCl, depending on *p*H of the medium. Free chlorine has been detected in strong acid medium in presence of chloride ion.

Although oxidation of bio-organic compounds by CAT has been reported, only a few reactions of amino acids in alkaline medium[3] have been studied from a kinetic view point. As a part of our kinetic studies of chloraminometric reactions in acid medium[4] we report our detailed investigations of oxidation of leucine, serine, glutamine and glutamic acid by CAT in presence of perchloric acid.

Experimental

All solutions were prepared in triply distilled water. Chloramine-T (E. Merck) was purified by the method of Morris *et al*[5]. An aqueous solution of the compound was iodometrically standardised and preserved in brown bottles to prevent its photochemical deterioration.

Leucine, serine, glutamine and glutamic acid (Centron Research Lab., Bombay, India) were found to be chromatographically pure. They were further assayed by the acetous perchloric acid method[6]. All other reagents were of accepted grades of purity. The ionic strength of the reaction mixture was kept constant at a high value with a concentrated solution of sodium perchlorate.

The reaction was carried out in glass stoppered pyrex boiling tubes. Requisite amounts of the amino acid, $HClO_4$ and $NaClO_4$ solutions and water (to maintain total volume constant for all runs), were taken in the tube and thermostated at 30°. A measured amount of CAT solution also at the same temperature was added to the mixture and progress of the reaction was followed by an iodometric estimation of the unreacted CAT in a measured aliquot of the reaction mixture at various time intervals. The course of the reaction was studied for two-half lives. The pseudo first order rate constants calculated were reproducible within ±2.0%.

Stoichiometry :

Varying ratios of amino acid to CAT were mixed in presence of $HClO_4$ ($\sim 0.5M$) at room temperature. Estimation of unreacted CAT after twenty-four hours showed that one mole of serine consumes three moles of CAT and one mole of leucine, glutamine or glutamic acid requires two moles of the oxidant :

$R'-CH(NH_2).COOH + 2\,RNCl\;Na \longrightarrow R'-CN + 2RNH_2 + CO_2 + 2NaCl$ $OH.CH_2.CH(NH_2).COOH + 3RNCl\;Na + H_2O \rightarrow 3RNH_2 + OHCH_2CNO + CO_2 + 3NaCl$ where : R' is $-(CH_3)_2$ for leucine, $-NH_2CO(CH_2)_2$ for glutamine and $-HOOC(CH_2)_2$ for glutamic acid ; and $R = H_3CC_6H_4SO_2$.

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Paper chromatography was used to identify the sulphonamide. Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution in ethanol as the spray reagent ($R_F = 0.905$). The nitriles were identified by their colour reaction with hydroxylamine and ferric chloride[7]. The cyanate formed was detected by Werner's test[8].

Results and Discussion

The kinetics of oxidation of amino acids by CAT was investigated at several initial concentrations of the reactants. At constant $[H^+]$, with the substrate in large excess the pseudo first order rate constant k_1 increase with [amino acid] and a first order dependence on the substrate concentration is noted (Table 1) (Fig. 1). The rate decreases with increasing $[HClO_4]$ (Table 2). A plot of log k_1 vs log $[H^+]$ gives a straight line with slope, −1 (Fig. 2).

TABLE 1—EFFECT OF CONCENTRATION OF REACTANTS ON THE REACTION RATE AT 30°C

$[H^+] = 0.05M$ for leucine and glutamine, $0.03M$ for serine and $0.01M$ for glutamic acid $\mu = 0.500M$

Amino acids (1)	[CAT]M (2)	[Amino acid]M (3)	$k_1 \times 10^4$ sec^{-1} (4)	k_2 mole^{-1} lit. sec^{-1} (5)
	0.003	0.02	1.44	7.201×10^{-3}
	0.003	0.025	1.89	7.544×10^{-3}
	0.003	0.035	2.69	7.686×10^{-3}
	0.003	0.040	2.98	7.449×10^{-3}
	0.003	0.060	4.10	6.848×10^{-3}
	0.003	0.03	2.54	8.467×10^{-3}
Leucine	0.0025	0.03	2.55	
	0.003	0.03(a)	2.56	
	0.0035	0.03	2.57	
	0.004	0.03	2.61	
	0.003*	0.03	2.56	
	0.003**	0.03	2.49	
	0.003	0.01	1.44	1.441×10^{-2}
	0.003	0.02	2.81	1.404×10^{-2}
	0.003	0.03(a)	4.25	1.417×10^{-2}
	0.003	0.04	6.86	1.465×10^{-2}
	0.003	0.05	7.29	1.458×10^{-2}
Serine	0.001	0.03	4.22	1.406×10^{-2}
	0.002	0.03	4.16	
	0.004	0.03	4.11	
	0.005	0.03	4.08	
	0.003*	0.03	4.22	
	0.003**	0.03	4.24	
	0.003	0.05(a)	2.66	5.318×10^{-3}
	0.003	0.03	2.60	5.330×10^{-3}
	0.003	0.04	2.05	5.118×10^{-3}
	0.003	0.06	3.28	5.885×10^{-3}
	0.003	0.08	4.22	5.278×10^{-3}
Glutamine	0.004	0.05	2.65	
	0.002	0.05	2.58	
	0.001	0.05	2.69	
	0.005	0.05	2.71	
	0.003*	0.05	2.65	
	0.003**	0.05	2.70	
	0.001	0.03(a)	3.99	
	0.002	0.03	3.98	
	0.003	0.03	4.00	
	0.004	0.03	3.91	
	0.005	0.03	3.88	
Glutamic acid	0.001	0.015	2.16	1.440×10^{-2}
	0.001	0.03	3.99	1.330×10^{-2}
	0.001	0.04	4.88	1.220×10^{-2}
	0.001	0.05	6.94	1.388×10^{-2}
	0.001	0.06	8.80	1.388×10^{-2}
	0.001*	0.03	4.04	
	0.001**	0.03	3.99	

* When $\mu = 2.0M$.
** In presence of excess of TSA.
(a) Standard runs.

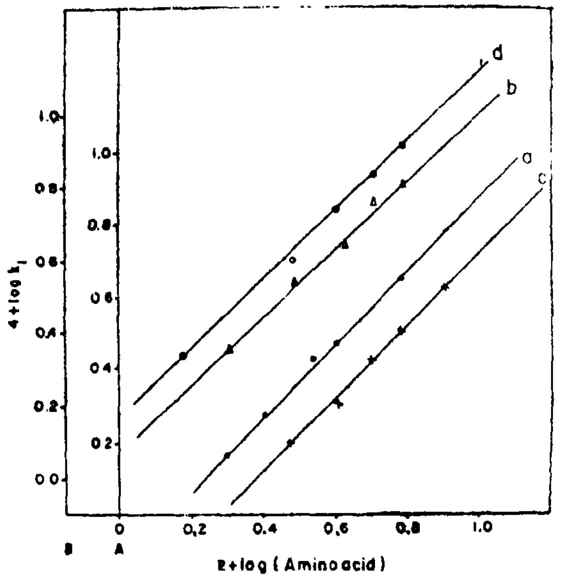


Fig. 1. Plot of log k_1 Vs [Amino acid].

(a) leucine, (b) serine, (c) glutamine and (d) glutamic acid. Scale A is for serine (b), glutamine (c), and leucine (a). Scale B is for glutamic acid (d).

$[CAT] = 0.003M$ for leucine, serine and glutamine and $0.001M$ for glutamic acid.

$[H^+] = 0.05M$ for leucine and glutamine, $0.03M$ for serine and $0.01M$ for glutamic acid.

$\mu = 0.5M$; Temperature = 30°.

TABLE 2—EFFECT OF ACID CONCENTRATION ON THE REACTION RATE AT 30°C

[Amino acid] = $0.03M$ for leucine, serine and glutamic acid, $0.05M$ for glutamine ; [CAT] = $0.003M$ for leucine, serine and glutamine, $0.001M$ for glutamic acid $\mu = 0.500M$

Amino acid (1)	$[H^+]M$ (2)	$k_1 \times 10^4$ sec^{-1} (3)	$10^5 k_1[H^+]$ mole^{-1} sec^{-1} (4)
	0.03	4.19	1.26
	0.05	2.56	1.28
Leucine	0.06	2.14	1.28
	0.07	1.88	1.32
	0.08	1.60	1.28
	0.03	4.25	1.28
	0.04	3.11	1.24
Serine	0.05	2.55	1.28
	0.06	1.97	1.18
	0.08	1.47	1.18
	0.025	5.48	1.36
	0.03	4.57	1.37
	0.05	2.66	1.33
Glutamine	0.06	2.29	1.37
	0.075	1.82	1.38
	0.10	1.34	1.34

(*Table 2 Contd.*)

	0.005	7.79	0.39
	0.006	6.59	0.39
Glutamic acid	0.007	5.86	0.39
	0.009	4.36	0.39
	0.010	3.99	0.39

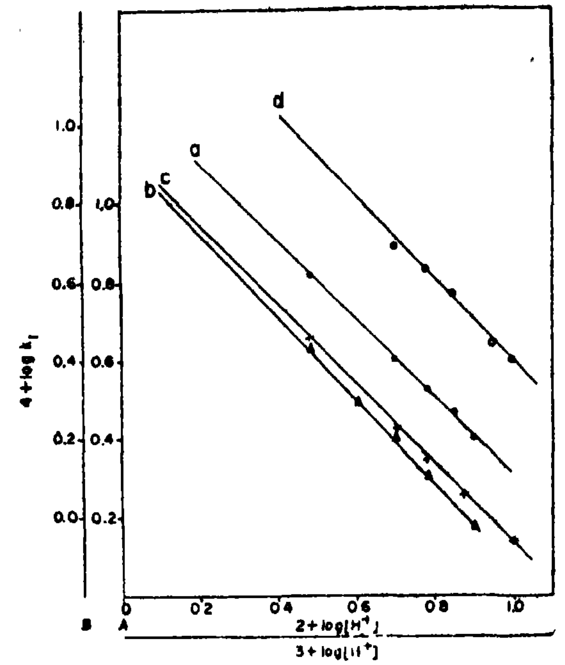


Fig. 2. Plot of log k_1 Vs log [H^+]

(a) leucine, (b) serine, (c) glutamine and (d) glutamic acid.

*[CAT] = 0.003*M* for leucine, serine and glutamine and 0.001*M* for glutamic acid.

[Amino Acid] = 0.03*M* for leucine, serine and glutamic acid and 0.05*M* for glutamine.

*Scale A for serine (b) and glutamine (d) ;

Scale B for leucine (a) and Scale C for glutamic acid (c)

μ = 0.5*M* ; Temperature = 30°.

The reaction was studied at different temperatures and the activation parameters have been evaluated (Table 3).

Table 3—Thermodynamic Parameters for the Oxidation of α-Amino acids by Chloramine-T in $HClO_4$ Medium

Amino acids	$\Delta H^{\#}$ KJ mol^{-1}	$\Delta S^{\#}$ JK^{-1}
Leucine	83.92±0.01	−26.87±0.01
Serine	99.28±0.03	+29.58±0.03
Glutamine	86.26±0.01	−23.28±0.02
Glutamic acid	67.36±0.02	−22.06±0.02

Concentrations of the reagents as in the standard runs (Table 1)

Effect of changing the solvent composition :

Addition of methanol to the reaction mixture decreases the rate. A plot of log k_{obs} vs 1/D where D is the dielectric constant gives a straight line with a negative slope (Fig. 3).

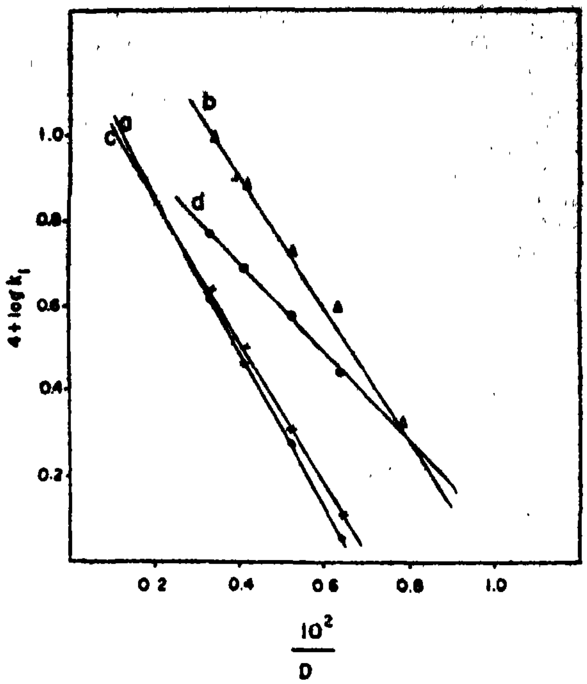


Fig. 3. Plot of log k_1 Vs 1/D

(a) leucine, (b) serine, (c) glutamine and (d) glutamic acid.

[CAT] = 0.003*M* for leucine, serine and glutamine ; and 0.001*M* for glutamic acid.

[Amino acid] = 0.03*M* for leucine, serine and glutamic acid and 0.05*M* for glutaine.

[H^+] = 0.05*M* for leucine and glutamine, 0.03*M* for serine and 0.01*M* for glutamic acid.

μ = 0.5*M* ; Temperature = 30°.

The experimental rate law is of the form :

$$-\frac{d}{dt}[CAT] = k\frac{[CAT][\text{Amino acid}]}{[H^+]} \quad \ldots (1)$$

Chloramine-T is a strong electrolytes[9]. (RNClNa, where $R = p\text{-}CH_3C_6H_4SO_2$) and the anion can be protonated in acid solutions (Equation 2). The free acid can undergo disproportionation and/or hydrolysis (Equations 3 and 4).

$$RNCl^- + H^+ \overset{K}{\rightleftharpoons} RNHCl \quad \ldots (2)$$

$K = 3.6 \times 10^4$ at 25°[10]

$$2\,RNHCl \overset{K_d}{\rightleftharpoons} RNCl_2 + RNH_2 \quad \ldots (3)$$

$K_d = 6.1 \times 10^{-2}$ at 25°[10]

$$RNHCl + H_2O \overset{K_h}{\rightleftharpoons} RNH_2 + HOCl \quad \ldots (4)$$

$K_h = 4.9 \times 10^{-8}$ at 25°[10].

Thus in acidified CAT solutions, the probable oxidising species are RNHCl, $RNCl_2$ (dichloramine-T) and HOCl. If $RNCl_2$ were to be the reactive species, then the rate law predicts a second order dependence of rate on CAT, which is contrary to the experimental observations. Ionic strength of the medium has no effect (Table 1) on the rate indicating that neutral species are involved in the rate determining step. Equation (4) indicates that the hydrolysis is slight and if HOCl is involved, a first order retardation of rate by added toluene sulphonamide is expected. However no such effect was noted. (Table 3) First approximation calculations by Bishop and Jennings[10] on decinormal solutions of CAT have shown that [RNHCl] and [HOCl] are $\sim 10^{-2}$ and $10^{-7}M$ respectively, around pH 0 – 1. Therefore RNHCl can be assumed as the reactive species under the present investigations.

An α-amino acid is known to exist in the following equilibria in aqueous solutions.

$$\underset{\substack{(SH^+)\\ \text{Cation}}}{RCH(NH_3^+)COOH} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\substack{(S)\\ \text{Aminoacid}}}{RCH(NH_2)COOH} \rightleftharpoons$$

$$\underset{\substack{(S^-)\\ \text{Anion}}}{RCH(NH_2)COO^-} + H^+ \rightleftharpoons \underset{\substack{(S^0)\\ \text{Zwitter ion.}}}{RCH(NH_3^+)COO^-}$$

Under the present experimental conditions the concentration of anion form will be very low and hence the possible reducing species may be either the cation form of amino acid or its zwitter ion S^0. With the cation as the active species the derived rate law predicts a direct dependence on $[H^+]$ which is contrary to experimental evidence. Hence assuming S^0 as the active species in the present investigations, Scheme-1 can be proposed to account for the observed kinetics.

$$SH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S^0 + H^+ \text{.......(a) ; Slow.}$$

$$S^0 + RNHCl \xrightarrow{k_2} X(\text{Intermediate})\text{...(b), Slow and rate determining.}$$

$$X + n\ RNHCl \xrightarrow{k_3} \text{products......(c) ; Fast}$$

n = 1 for leucine, glutamine and glutamic acid.

n = 2 for serine.

SCHEME—I

Applying steady state treatment to X and S^0 and with the reasonable assumption that $k_{-1}[H^+] \gg k_2$ [RNHCl], the rate law

$$-\frac{d}{dt}[CAT] = \frac{k_1k_2[SH^+][RNHCl]}{k_{-1}[H^+]} \quad \dots \dots (5)$$

can be derived in agreement with Equation (1).

Effect of changing solvent composition :

In the present investigations a plot of log k_{obs} vs 1/D (D = Dielectric constant) gives a straight line (Fig. 3) with a negative slope indicating[11,12] that CAT is reacting in neutral form and this supports the dipole-dipole interaction of Scheme—I.

Effect of chloride ion :

It is interesting to note that addition of chloride ion increases the rate of reaction. Such behaviour has been noticed in the Orton rearrangement of organic haloamines[10]. The following scheme can explain the observed kinetics :

$$SH \overset{k_1}{\rightleftharpoons} S^\circ + H^+ \quad \dots (i)$$

$$RNHCl + H_2O \overset{k_h}{\rightleftharpoons} RNCl^- + H_3O^+ \quad \dots (ii)$$

$$RNHCl + Cl^- \overset{k}{\rightleftharpoons} X \quad \dots (iii)$$

$$X + S^\circ \xrightarrow{k_4} X' \quad \dots (iv)$$

$$X' + RNHCl \xrightarrow{k_5} \text{Products} \quad \dots (v)$$

SCHEME—II

If $[CAT]_T$ represents total concentration of CAT, then

$$\text{rate} = k_4[X][S^\circ]$$

$$= \frac{Kk_4[Cl^-][CAT]_T[S^\circ]}{1+K[Cl^-]}$$

$$= \frac{k_4Kk_1[Cl^-][CAT]_T[SH^+]}{[H^+]\{1+K[Cl^-]\}} \quad \dots (6)$$

Since observed rate law is

$$-\frac{d}{dt}[CAT] = k_{obs}\frac{[CAT][SH^+]}{[H^+]}$$

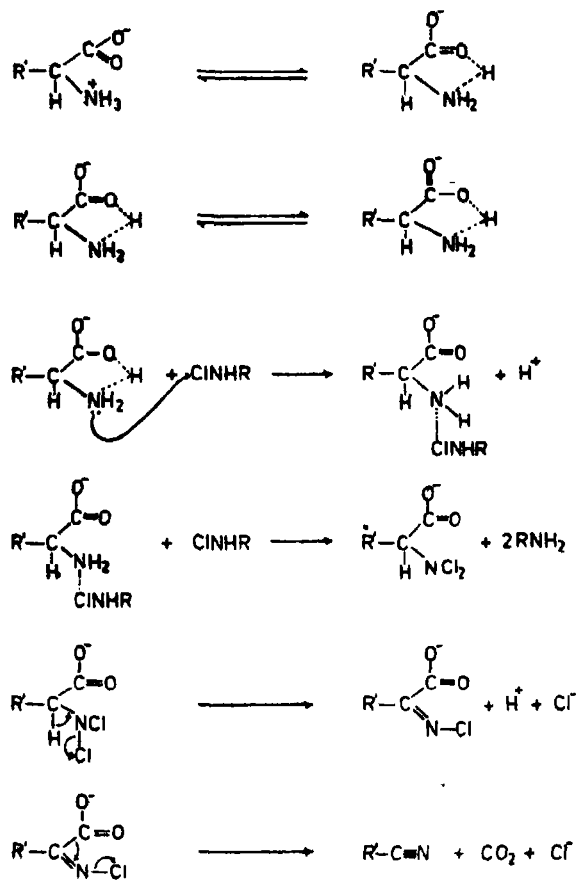
$$K_{obs} = \frac{k_4Kk_1Cl^-}{1+K[Cl^-]}$$

$$\text{or} \quad \frac{1}{k_{obs}} = \frac{1+K[Cl^-]}{k_4Kk_1[Cl^-]}$$

$$= \frac{1}{k_4Kk_1[Cl^-]} + \frac{1}{k_4k_1} \quad \dots (7)$$

A double reciprocal plot of $1/k_{obs}$ vs $1/[Cl^-]$ gives a straight line (Fig. 4).

A detailed mechanism of oxidation is given in Scheme III.



SCHEME III

The nitrile undergoes further reaction with the oxidant molecule and hydrolysis of the species would produce the cyanate.

The effect of H-bonding ensures considerable electron density at the amine nitrogen through the release of its non-bonding electrons. The enhanced nucleophilicity at the N-atom facilitates an electrophilic attack by the positive chlorine of RNHCl. This is more or less concerted with the release of H^+ ion and subsequent reactions take place through fast steps.

The mechanism is further supported by the fairly large values of the energy of activation for the formation of a more compact chlorinated amino acid activated complex. The negative entropy of activation observed during these reactions supports this concention. The values of thermydynamic

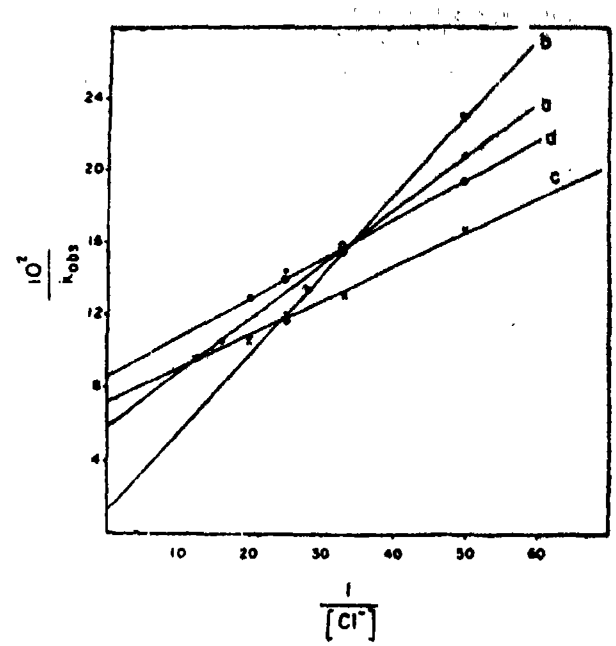


Fig. 4. Plot of log $\frac{1}{K_{obs}}$ Vs $\frac{1}{[Cl^-]}$.

(a) leucine, (b) serine, (c) glutamine and (d) glutamic acid.

[CAT] 0.003*M* for leucine, serine and glutamine and 0.001*M* for glutamic acid.

[Amino acid] = 0.08*M* for leucine, serine and glutamic acid and 0.05*M* for glutamine.

$[H^+]$ = 0.05*M* for leucine and glutamine, 0.08*M* for serine and 0.01*M* for glutamic acid.

μ = 0.5*M* ; Temperature = 30°.

parameters are comparable to those obtained during the oxidation of glycine and valine[4] by CAT.

Acknowledgement

One of us (S. N. K.) acknowledges a research fellowship from University Grants Commission, New Delhi, under the Faculty Improvement Programme.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1191-1193

Kinetics and Catalysis of Thermal Decomposition of Potassium Chlorate and Potassium Bromate—A Thermogravimetric Study

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Manuscript received 18 December 1979, revised 30 June 1980, accepted 25 August 1980

A comparative study of the kinetics and mechanism of thermal decomposition of potassium chlorate and potassium bromate catalysed by CuO and MnO_2 has been made by dynamic thermogravimetry. The kinetic parameters for the processes, based on Coats-Redfern equation and mechanistic equations, have been determined. The MnO_2 catalysed decomposition of $KClO_3$ proceeds by Mampel mechanism, while that of $KBrO_3$ satisfies the Avrami mechanism.

THE technical importance of thermal decomposition of oxyhalogen salts has attracted considerable attention in recent years[1-6]. In the present paper, kinetics of uncatalysed, and metal oxide-catalysed thermal decomposition of potassium chlorate and potassium bromate have been discussed on the basis of mechanistic and mechanism non-invoking equations. The mechanism-based study was made by choosing different functional forms of α (fractional decomposition), assumed to be governing the rate controlling processes and fitting them into MacCallum-Tanner equation[7]. The mechanism-non-invoking treatment-was based on the Coats-Redfern equation[8].

Experimental

Potassium chlorate ('Baker Analysed' Reagent grade) and potassium bromate (M & B grade) were dried at 120° for several hours and kept in desiccator before use. The metal oxides, *viz*., CuO and MnO_2 used were of BDH grade, and had purity above 98%. The oxides were ignited at 500° and kept in desiccator before use. The metal oxides and oxysalts were of mesh size 200-240. In all experiments 0.2 g sample of the salts was mixed intimately with 50 mg of the oxide before taking TG traces.

The TG traces were taken in a Stanton recording thermobalance (model TR-I). Heating rate was 4° min^{-1} and the atmosphere was static air The amount of KBr and KCl left behind in all the experiments agreed well with the calculated values and the instrument reading.

Results and Discussion

The total weight loss in all cases were 78 ± 1 mg for $KClO_3$ and 58 ± 1 mg for $KBrO_3$. For purpose of brevity, the TG traces, redrawn as mass versus temperature, and the DTG curves are not shown. Excepting the catalysed decomposition of $KClO_3$ by CuO, the other catalysed processes proceeded to completion immediately after reaching the peak temperature of decomposition (Ts). In such cases the α values were taken only upto the peak temperature of decomposition. The temperature range of decomposition of potassium chlorate mixed with CuO had a greater spread ($T_f - T_i = 140°$), whereas that for the other catalysed decompositions was considerably less as revealed by Table 1 ; T_f and T_i being the temperatures of completion and initiation respectively of the process. An increase in the temperature span for the decomposition of the system, $KClO_3$-CuO has been reported previously also[4]. The effects of the metal oxides were not then explained on the basis of change in E*, ΔS^* etc. (where E* and ΔS^* are energy and entropy of activation), but explanations were based on the catalysts' influence on melting of the substrate and their semiconductive properties. It could be that the phenomenon be specific in nature with respect to the catalyst substrate system. The more ordered configuration of the transition state, when CuO is present (as shown by the change in ΔS^*), and the large decrease in E* while the mechanistic mode remained unchanged can result in a slower enhancement of rate with increase in temperature. (In the case of $KBrO_3$ there is change in the mechanism itself compared to the uncatalysed decomposition, when it occurs in presence of CuO). In all the cases where metal oxides were used the T_i, T_s and T_f values were lowered substantially.

The TG data of all the decompositions fitted well into the Coats-Redfern equation for first order process. The Coats-Redfern plots, and the plots based on mechanistic equations, excepting the mechanistic plots for the decomposition of $KBrO_3$ are not given. The frequency factors, energies and

TABLE 1

System	T_iK	T_sK	T_fK	Temperature range of decomposition
$KClO_3$	773	868	893	120°
$KBrO_3$	643	698	723	80
$KClO_3 + CuO$(25% w/w)	578	663	718	140
$KBrO_3 + CuO$(25% w/w)	583	645	648	65
$KClO_3 + MnO_2$(25% w/w)	553	608	613	60
$KBrO_3 + MnO_2$(25% w/w)	573	625	633	60

entropies of activation etc. for the decomposition of $KClO_3$ and mixtures of $KClO_3$ with CuO and with MnO_2 were calculated using the Coats-Redfern equation and mechanism based equations. These are given in Table 2. The corresponding values for the potassium bromate decomposition based on Coats-Redfern equation were taken from elsewhere[6] and those based on mechanistic equations were calculated.

Generally the mechanism based study has been applied to isothermal weight change processes only. However, recently there have been extensions of this approach to dynamic thermogravimetric studies also[8]. The fractional decomposition, α, and the rate of solid state decomposition reaction are related by the general equation, $\frac{d\alpha}{dt} = k.f(\alpha)$, where $f(\alpha)$ is a function of α given by the rate controlling process and $k = Ze^{-E^*/RT}$, (Z being frequency factor and E^*, activation energy). The integral,

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha), \text{ and}$$

$g(\alpha)$ can have different forms for different mechanistic models[8]. In the present study six different model forms of $g(\alpha)$ have been employed *viz.*,

$$\alpha^2,\ [1-(1-\alpha)^{1/3}]^2,\ [-\ln(1-\alpha)],$$
$$[-\ln(1-\alpha)]^{1/2}, [-\ln(1-\alpha)]^{1/3} \text{ and } 1-(1-\alpha)^{1/3}.$$

Plots of log $g(\alpha)$ values vs $\frac{1}{T}$ is linear only for the log $g(\alpha)$ that corresponds to the probable rate controlling process[8]. When more than one such linear plots are obtainable for different forms of $g(\alpha)$ plotted against $\frac{1}{T}$, the probable operating mechanism can be selected by comparing the values of E^*, Z etc. from such plots with those obtainable from mechanism non-invoking general kinetic study.

In the present study we used the MacCallum-Tanner equation of the form :

$$\log g(\alpha) = \log \frac{ZE^*}{\phi R} - 0.48E^{*0.44} - \left(\frac{0.449+0.217E^*}{T}\right) \times 10^3$$

(where ϕ is heating rate) for evaluating E^* and Z from such linear plots. Representative plots showing the influence of the function $g(\alpha)$ on the plot of log $g(\alpha)$ vs $\frac{1}{T}$ is given in Fig. 1. In cases where more than one such linear plots were obtained, the probable operating mechanism was selected by comparing the values of E^* and Z obtained from log $g(\alpha)$ vs $\frac{1}{T}$ plots with those obtained from the Coats-Redfern equation. It may be pointed out here that in this case the $g(\alpha)$ employed in the Coats-Redfern equation has the form, ln $w_\alpha/w_\alpha - w$ (where w_α is mass loss at completion of the reaction and w is mass loss at temperature T), which is equivalent to $[-\ln(1-\alpha)]$. The values of E^*, Z and ΔS^* and the probable operating mechanism are given in Table 2.

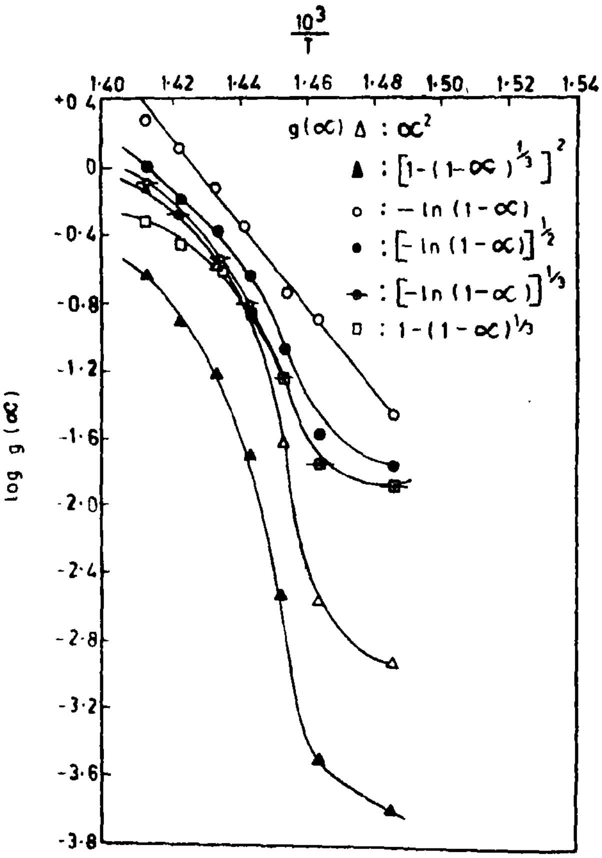


Fig. 1. Mechanistic plots :—log $g(\alpha)$ versus $\frac{10^3}{T}$ for the decomposition of $KBrO_3$.

It is interesting to note that the CuO catalysed decomposition of $KClO_3$ and $KBrO_3$ have similar mode of decomposition, in view of the similarities in the activation parameters and frequency factor. In either case there is marked decrease in activation

TABLE 2

System	Coats-Redfern equation			Mechanistic equation		
	E*K.J $mole^{-1}$	Z. sec^{-1}	ΔS* J $mole^{-1}$ K^{-1}	E*K.J $mole^{-1}$	Z. sec^{-1}	Equation applicable
$KClO_3$	363.1	2.45×10^{21}	155.8	317.3	2×10^{18}	Avrami
$KBrO_3$	433.0	9.4×10^{28}	310.8	469.0	1.8×10^{24}	Mampel
$KClO_3+CuO$(25% w/w)	177.4	3.55×10^{11}	−35.0	168.5	2.48×10^{13}	Avrami
$KBrO_3+CuO$(25% w/w)	168.0	3.8×10^{10}	−48.8	157.0	7.3×10^{10}	Avrami
$KClO_3+MnO_2$(25% w/w)	420.1	1.21×10^{26}	325.1	418.6	8.7×10^{27}	Mampel
$KBrO_3+MnO_2$(25% w/w)	186.0	7.94×10^{12}	− 4.1	164.9	1.86×10^{13}	Avrami

energy and the entropy of activation becomes considerably less, and have comparable values (Table 2). The decrease in activation entropy suggests the possibility of formation of chemisorbed transition state, the catalysis being due to lowering of activation energy. The mechanism found probable for both the cases are the Avrami[10] model equation, *viz*, $1-(1-\alpha)^{1/3}$ for $g(\alpha)$. The probable rate controlling process would be phase boundary reaction assuming spherical symmetry. This is so in the decomposition of $KBrO_3$ mixed with MnO_2 also. However, the decomposition of $KClO_3$ in the presence of MnO_2 showed interesting departure from this trend. The acceleration in rate seems to be purely an entropy effect as there is more than a two fold increase in $\triangle S^*$ compared to the uncatalysed decomposition, in spite of marginal increase in activation energy. A similar behaviour was reported[6] for the thermal decomposition of potassium bromate mixed with TiO_2. It appears therefore that MnO_2 catalyses the decomposition by increasing the disorder of the transition state considerably. The mode of this decomposition according to mechanistic treatment was found to follow the Mampel[11] equation i.e., $-\ln(1-\alpha)$ for $g(\alpha)$. The reaction proceeds by a random nucleation process, that is, with formation of a nucleus on every particle. The normal decomposition of $KClO_3$ was found to follow the Avrami model equation with phase boundary reaction and that of $KBrO_3$ to follow the Mampel model equation assuming random nucleation.

Acknowledgement

The authors are thankful to Dr. S. S. Moosath, Head of the Department for providing facilities.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1194-1199

Third Dissociation Constant of Phosphoric Acid from 283.15 K to 323.15 K

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Manuscript received 6 August 1980, accepted 9 September 1980

Third dissociation constant of phosphoric acid has been determined from 283.15K to 323.15K in steps of 5K by finding the hydrolysis constant K_h of HPO_4^{2-}. pK_h has been determined from e.m.f. measurement of cell (C—1) utilising modified Davies equation.

$$H_2, (Pt) \mid Na_2HPO_4, NaOH, NaCl, AgCl \mid Ag \quad \cdots \quad (C—1)$$

Between 283.15K and 323.15K, pK_3 fits in the equation, $pK_3 = \frac{2397.4}{T} + 4.2364 - 2.6061 \times 10^{-2}T + 8.3834 \times 10^{-5}T^2$. The thermodynamic quantities ΔH_3°, ΔG_3°, ΔS_3° and ΔCp_3° have also been determined at these temperatures. At 298.15K these values are 5175J mol^{-1}, 68264J mol^{-1}, -212J mol^{-1}K^{-1} and -559J mol^{-1}K^{-1} respectively.

ACCURATE values of the third dissociation constant of phosphoric acid over a number of temperatures are not known. A number of workers have determined pK_3 either at one (mostly 298.15K) or two temperatures or rather at high *ionic strength*. Chief among these determinations are recorded in Table 1.

TABLE 1—pK_3 OF PHOSPHORIC ACID

Method	pK_3	Temp/K	Reference
Conductivity and distribution ratio of ammonium phosphate	11.89	298.15	1
Potentiometric titration	12.30	291.15	2
*p*H of a mixture of sec. and tert. phosphates	12.66	311.15	3
e.m.f. of quinhydrone-calomel cell	12.10	298.15	4
Hydrolysis of tert. phosphate	11.99	298.15	5
	11.83	311.15	
e.m.f. of cells with liquid junction potential	12.325	298.15	6
*p*H	11.83	311.15	7
Colorimetry	11.70 to 11.95	298.15	8
Spectrophotometric study of mixtures of $Na_2CO_3 - NaHCO_3$ and $Na_2HPO_4 - NaOH$	12.375	298.15	9
Laser study of solution of orthophosphates of Na and K	11.921	298.15	10

Many of these pK_3 values do not correspond to thermodynamic dissociation constant. Neither the pK_3 values nor the thermodynamic quantities corresponding to the third stage of dissociation of phosphoric acid are known at a number of temperatures.

This led us to study cell (C – 1).

$$H_2, (Pt) \mid Na_2HPO_4(m_1), NaOH(m_2), NaCl(m_3), AgCl \mid Ag \quad \ldots \quad (C-1)$$

It was observed that when $m_1 : m_3 = 1 : 1$, the Ag/AgCl, Cl^- electrode was sluggish and the bias potential went on increasing with time. The bias potential decreased when $m_1 : m_3 = 1 : 2$ and disappeared altogether when $m_1 : m_3 = 1 : 3$. It seemed that the bias potential was due to slow adsorption of phosphate on Ag/AgCl electrodes which was prevented when Cl^- concentration increased. So $m_1 : m_3$ was kept equal to 1 : 3 while $m_1 : m_2$ had to be kept between 1 : 6 to 1 : 8 to have an adequate concentration of PO_4^{3-}. The stoichiometric concentrations were correct to a micromol kg^{-1}.

Experimental

$Na_2HPO_4.2H_2O$, NaOH and NaCl used for the preparation of solutions were each G.R. samples of E. Merck. Their purities were checked by standard methods[11]. All solutions were prepared in doubly distilled water of conductivity $<0.5 \times 10^{-6}$ ohm^{-1} cm^{-1}. Carbonate-free NaOH solution was kept in polythene bottles in an atmosphere of N_2 until use. NaCl was found free from bromide and iodide[12]. Two stock solutions were prepared—*solution 'A' containing Na_2HPO_4 and NaCl in* mole ratio of 1 : 3 and solution 'B' was a standard solution of carbonate-free NaOH kept in an atmosphere of N_2. Experimental solutions were prepared by taking weighed amounts of 'A' and 'B' and diluting the mixture appropriately in a weighed measuring flask. All weighings were corrected for buoyancy.

The experimental solutions were deoxygenated by passing pure presaturated N_2 for 12 to 14 hours and were then introduced under pressure of N_2 into

the conventional 'H'-shaped electrode vessel. One limb of the electrode vessel was fitted up with Ag/AgCl electrode. The other limb also contained the experimental solution but no electrode to begin with. Previous to filling up the electrode vessel with experimental solution, it was completely flushed out with pure presaturated N_2. Ag/AgCl electrodes were prepared by thermal electrolytic[13] method and hydrogen electrodes were prepared according to standard methods[14]. A cushion of N_2 gas was allowed to remain between the stopper of the limbs containing Ag/AgCl, Cl^- electrodes and the solution. The stopper of the interconnecting tube was then closed and the electrode vessel together with the presaturators were thermostated at ± 0.05K. Electrolytic H_2 gas supplied by Indian Oxygen Ltd. was passed successively through a column filled with KOH pellets, a 30 cm × 2 cm column of reduced copper heated to *ca* 780 K, another column of KOH pellets, a sintered glass plate of pore size G 0 and then through two presaturators. Pure and presaturated H_2 gas thus obtained was bubbled through the other limb at the rate of 3 or 4 bubbles per sec. A slower rate of bubbling took a long time to produce equilibrium. After two hours hydrogen electrodes rinsed with the experimental solution were introduced in the other limb. Thereafter e.m.f. reading was taken every half an hour after opening the interconnecting stop cock. A Tinsley Vernier potentiometer (type 4363) coupled with a Bajaj galvanometer of sensitivity 3.92×10^{-10} amp mm^{-1} was used for the purpose. E.M.F.'s were compared against a certified Weston cadmium cell of Cambridge Instrument Co. Constant e.m.f. values were obtained after 5 to 6 hours of the introduction of hydrogen electrode Duplicate cells were set up. The e.m.f. values recorded in Tables 2 to 10 are the mean of the duplicate readings after applying correction for barometric pressure, vapour pressure and bubbler depth[15]. The e.m.f. of the duplicate cells agreed within 0.05 mV. The molalities of the various ionic species were found as discussed below.

Results and Discussion

The e.m.f. of cell (C-1) is given by $E = E^\circ - k \log m_H . m_{Cl}$, where $k = \frac{2.3026RT}{F}$. This equation may be written as $E = E^\circ - k \log \frac{K_w}{a_{OH}} . a_{Cl}$, since $K_w = a_H . a_{OH}$ as a_{H_2O} is taken to be unity for dilute solutions. Or,

$$E = E^\circ - k \log K_w - k \log \frac{m_{Cl}}{m_{OH}} - k \log \frac{\gamma_{Cl}}{\gamma_{OH}} \quad \ldots (1)$$

In a previovs communication[16] we found that modified Davies equation may be taken to be valid in alkaline solution. So, applying modified Davies equation to (1) we get,

$$\log m_{OH} = \frac{(E - E^0)}{k} + \log K_w + \log m_{Cl} + (\beta_{Cl} - \beta_{OH})\mu \quad \ldots (2)$$

In cell solution of cell (C-1) when the m_{OH} is much greater than $m_{HPO_4^{2-}}$ it is presumed that the reaction (3) takes place,

$$HPO_4^{2-} + OH^- \rightleftharpoons PO_4^{3-} + H_2O \quad \ldots (3)$$

The ionic strength μ is given by equation (4).

$$\mu = 3m_1 + m_2 + m_3 + 2x \quad \ldots (4)$$

where $x = m_{PO_4} = m_2 - m_{OH}$

The hydrolysis of PO_4^{3-} is represented in equation (3). Assuming a_{H_2O} to be unity,

$$K_h = \frac{m_{HPO_4} . m_{OH}}{m_{PO_4}} \times \frac{\gamma_{HPO_4} . \gamma_{OH}}{\gamma_{PO_4}} \quad \ldots (5)$$

Henceforth charges are left out for neatness. Putting

$K_H = \frac{m_{HPO_4} . m_{OH}}{m_{PO_4}}$ and applying modified Davies equation to (5) we get,

$$\log K_h = \log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} - \beta'_s \mu$$

which on transformation is reduced to (6).

$$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_h + \beta'_s \mu \quad \ldots (6)$$

where $\beta'_s = (\beta_{PO_4} - \beta_{HPO_4} - \beta_{OH})$.

Now taking $\mu = 3m_1 + m_2 + m_3$ and utilising the values of $(\beta_{Cl} - \beta_{OH})$ and K_w reported elsewhere[16] we get a value of m_{OH} from equation (2). The values of k, E^0 and A required for this purpose is obtainable from literature[17-19]. This value of m_{OH} is now substituted in equation (4) to get a value of 'x' and hence a new value of μ. The process of iteration is repeated till we get constant and consistent values of m_{OH}, m_{HPO_4}, m_{PO_4} and μ correct to a micromol kg^{-1}. The values of K_H are then calculated. These values have been recorded in Tables 2 to 10.

Plots of L.H.S. of equation(6) against μ (some of which are shown in Fig. 1) at all the temperatures studied were straight lines—the maximum deviation of the points being less than 0.03 mV. The intercept of the lines on extrapolation to $\mu = 0$ give values of $\log K_h$ and the slopes give β'_s. These values were also obtained statistically from least square analysis and are tabulated in Table 11. Both the values agreed closely with one another. pK_3 was now obtained from equation (7).

$$pK_3 = pK_w - pK_h \quad \ldots (7)$$

TABLE 2

Temp. 283.15K — Stoichiometric Molalities and Ionic Strengths in Cell (C – 1)

$m_{Na_2HPO_4}$	m_{NaOH}	m_{NaCl}	E in abs. volt	m_{HPO_4}	m_{OH}	m_{PO_4}	μ	$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.002398	0.016868	0.007196	1.06396	0.0003188	0.018784	0.002079	0.034433	$\bar{3}.635$
0.003195	0.023518	0.009587	1.06672	0.0002760	0.020594	0.002919	0.048523	$\bar{3}.648$
0.003981	0.027552	0.011944	1.06495	0.0003175	0.023889	0.003663	0.058764	$\bar{3}.708$
0.004782	0.033366	0.014349	1.06510	0.0003289	0.028918	0.004453	0.070967	$\bar{3}.747$
0.005571	0.039725	0.016717	1.06569	0.0003215	0.034476	0.005249	0.083779	$\bar{3}.770$
0.007220	0.047294	0.021666	1.06317	0.0004028	0.040476	0.006818	0.104302	$\bar{3}.868$

TABLE 3

Temp. 288.15K — Cell (C – 1)

$m_{Na_2HPO_4}$	m_{NaOH}	m_{NaCl}	E in abs. volt	m_{HPO_4}	m_{OH}	m_{PO_4}	μ	$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.002401	0.017215	0.007205	1.06749	0.0004086	0.015223	0.001992	0.035607	$\bar{3}.812$
0.003188	0.019702	0.009566	1.06324	0.0005304	0.017045	0.002657	0.043145	$\bar{3}.876$
0.004022	0.024458	0.012068	1.06264	0.0005757	0.021012	0.003446	0.055548	$\bar{3}.927$
0.004807	0.030311	0.014425	1.06355	0.0.05828	0.026087	0.004224	0.067605	$\bar{3}.969$
0.005590	0.035833	0.016801	1.06395	0.0006785	0.030912	0.004921	0.079271	$\bar{2}.069$
0.006446	0.042832	0.019842	1.06492	0.0006670	0.037054	0.005779	0.093070	$\bar{2}.099$
0.007220	0.047294	0.021666	1.06447	0.0007275	0.040801	0.006493	0.103606	$\bar{2}.147$

TABLE 4

Temp. 293.15K — Cell (C – 1)

$m_{Na_2HPO_4}$	m_{NaOH}	m_{NaCl}	E in abs. volt	m_{HPO_4}	m_{OH}	m_{PO_4}	μ	$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.002401	0.017215	0.007205	1.06891	0.0005620	0.015876	0.001839	0.035301	$\bar{3}.991$
0.003188	0.019702	0.009566	1.06459	0.0007006	0.017215	0.002487	0.042805	$\bar{2}.031$
0.004022	0.024458	0.012068	1.06401	0.0007996	0.021236	0.003222	0.055035	$\bar{2}.105$
0.004807	0.030311	0.014425	1.06495	0.0008631	0.026367	0.003924	0.067045	$\bar{2}.176$
0.005599	0.035832	0.016801	1.06530	0.0009260	0.031160	0.004673	0.078777	$\bar{2}.223$
0.006446	0.042832	0.019342	1.06631	0.0009809	0.037366	0.005466	0.092444	$\bar{2}.296$
0.007220	0.047294	0.021667	1.0C587	0.0010823	0.041156	0.006138	0.102901	$\bar{2}.351$

TABLE 5

Temp. 298.15K — Cell (C – 1)

$m_{Na_2HPO_4}$	m_{NaOH}	m_{NaCl}	E in abs. volt	m_{HPO_4}	m_{OH}	m_{PO_4}	μ	$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.002390	0.017318	0.007172	1.07047	0.0006198	0.015547	0.001771	0.035202	$\bar{2}.057$
0.002984	0.022740	0.008955	1.07166	0.0005889	0.020345	0.002395	0.045489	$\bar{2}.056$
0.003982	0.028676	0.011950	1.06992	0.0007006	0.025395	0.003282	0.059136	$\bar{2}.132$
0.004766	0.033684	0.014301	1.06928	0.0006858	0.029604	0.004080	0.070448	$\bar{2}.124$
0.005951	0.038155	0.017856	1.06630	0.0008026	0.033007	0.005148	0.084158	$\bar{2}.174$
0.005941	0.043158	0.017829	1.06692	0.0007257	0.037942	0.005216	0.089242	$\bar{2}.190$
0.007164	0.047248	0.021602	1.06701	0.0008253	0.040909	0.006339	0.103001	$\bar{2}.220$

TABLE 6

Temp. 303.15K — Cell (C – 1)

$m_{Na_2HPO_4}$	m_{NaOH}	m_{NaCl}	E in abs. volt	m_{HPO_4}	m_{OH}	m_{PO_4}	μ	$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.002984	0.022740	0.008955	1.07345	0.001051	0.020807	0.019880	0.044452	$\bar{2}.415$
0.003982	0.028676	0.011950	1.07174	0.001336	0.026080	0.026465	0.057787	$\bar{2}.516$
0.004766	0.033684	0.014301	1.07118	0.015320	0.030450	0.032338	0.068681	$\bar{2}.585$
0.005951	0.038155	0.017856	1.06880	0.019890	0.034148	0.040116	0.081886	$\bar{2}.674$
0.005941	0.043158	0.017829	1.07185	0.018516	0.039068	0.040898	0.086991	$\bar{2}.715$
0.007164	0.047248	0.021502	1.06906	0.022932	0.042377	0.048710	0.099985	$\bar{2}.798$

TABLE 7

Temp. 308.15K | Cell (C – 1)

$m_{Na_2HPO_4}$	m_{NaOH}	m_{NaCl}	E in abs. volt	m_{HPO_4}	m_{OH}	m_{PO_4}	μ	$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.002432	0.014554	0.007323	1.06860	0.001250	0.013372	0.001182	0.031465	$\bar{2}$.463
0.003188	0.019946	0.009595	1.06955	0.001408	0.018171	0.001775	0.042601	$\bar{2}$.513
0.003975	0.024961	0.011967	1.06954	0.001686	0.022672	0.002289	0.053480	$\bar{2}$.611
0.004762	0.031346	0.014387	1.07071	0.001820	0.028405	0.002941	0.065852	$\bar{2}$.668
0.005569	0.035704	0.016768	1.06997	0·002108	0.032243	0.003461	0.076101	$\bar{2}$.741
0.006354	0.043322	0.020492	1.06977	0.002278	0.039246	0.004076	0.091028	$\bar{2}$.812
0.007594	0.049899	0.022863	1.07047	0.002689	0.044995	0.004905	0.105352	$\bar{2}$.899

TABLE 8

Temp. 313.15K | Cell (C – 1)

$m_{Na_2HPO_4}$	m_{NaOH}	m_{NaCl}	E in abs. volt	m_{HPO_4}	m_{OH}	m_{PO_4}	μ	$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.002480	0.018336	0.007437	1.07589	0.001408	0.017264	0.001072	0.035396	$\bar{2}$.686
0.003211	0.023391	0.009635	1.07538	0.001779	0.021959	0.001432	0.045491	$\bar{2}$.803
0.003953	0.028781	0.011863	1.07517	0.002015	0.026842	0.001938	0.055982	$\bar{2}$.846
0.004793	0.030540	0.014383	1.07141	0.002575	0.028322	0.002218	0.064363	$\bar{2}$.938
0.005637	0.035923	0.016916	1.07141	0.003039	0.033326	0.002598	0.074946	$\bar{1}$.040
0.006407	0.042278	0.019226	1.07233	0.003335	0.039205	0.003073	0.086870	$\bar{1}$.104
0.007208	0.047155	0.021629	1.07207	0.003767	0.043714	0.003441	0.096964	$\bar{1}$.181

TABLE 9

Temp. 318.15K | Cell (C – 1)

$m_{Na_2HPO_4}$	m_{NaOH}	m_{NaCl}	E in abs. volt	m_{HPO_4}	m_{OH}	m_{PO_4}	μ	$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.002480	0.018336	0.007437	1.07745	0.001588	0.017444	0.000892	0.035014	$\bar{2}$.824
0.003211	0.023391	0.009635	1.07686	0.001950	0.022131	0.012605	0.045170	$\bar{2}$.904
0.003953	0.028781	0.011863	1.07670	0.002280	0.027108	0.016730	0.055849	$\bar{2}$.971
0.004793	0.030540	0.014383	1.07275	0.002711	0.028458	0.020818	0.063877	$\bar{2}$.993
0.005637	0.035923	0.016916	1.07274	0.003203	0.033490	0.024338	0.074618	$\bar{1}$.097
0.006407	0.042278	0.019226	1.07368	0.003546	0.039417	0.028608	0.086472	$\bar{1}$.168
0.007208	0.047155	0.021629	1.07348	0.004098	0.044045	0.031094	0.096646	$\bar{1}$.264

TABLE 10

Temp. 323.15K | Cell (C – 1)

$m_{Na_2HPO_4}$	m_{NaOH}	m_{NaCl}	E in abs. volt	m_{HPO_4}	m_{OH}	m_{PO_4}	μ	$\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.002480	0.018336	0.007437	1.07877	0.001711	0.017568	0.000769	0.034702	$\bar{2}$.927
0.003211	0.023391	0.009635	1.07816	0.002092	0.022273	0.001118	0.044816	$\bar{2}$.984
0.003953	0.028781	0.011863	1.07801	0.002455	0.027282	0.001498	0.055502	$\bar{1}$.054
0.004793	0.030540	0.014383	1.07402	0.002926	0.028672	0.001867	0.068043	$\bar{1}$·079
0.005637	0.035923	0.016916	1.07400	0.003420	0.033706	0.002217	0.074185	$\bar{1}$.171
0.006407	0.042278	0.019226	1.07492	0.003739	0.039610	0.026680	0.086061	$\bar{1}$.227
0.007208	0.047155	0.021629	1.07680	0.004274	0.044221	0.029336	0.096274	$\bar{1}$.313

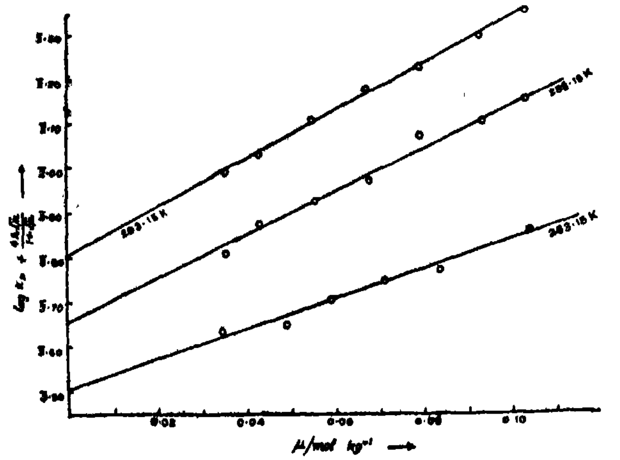


Fig. 1. Plot of $\log K_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$ against μ.

TABLE 11—pK_h OF PO_4^{3-} AND pK_3' OF H_3PO_4

Temp/K	pK_h	β'_3/mol^{-1} kg	pK_w	pK_3
283.15	2.495±0.019	3.33±0.27	14.533	12.043
288.15	2.345±0.021	4.84±0.29	14.350	12.005
293.15	2.195±0.010	5.33±0.11	14.170	11.979
298.15	2.040±0.023	2.59±0.25	14.002	11.962
303.15	1.885±0.009	6.81±0.12	13.842	11.959
308.15	1.725±0.014	6.00±0.18	13.690	11.957
313.15	1.580±0.024	7.95±0.35	13.462	11.957
318.15	1.490±0.021	6.92±0.30	13.398	11.977
323.15	1.285±0.015	6.16±0.21	13.263	11.971

These values of pK_3 are also recorded in Table 11. As the e.m.f. values are correct to ±0.025 mV the pK_3 are correct to 0.008 units.

The values of pK_3 obtained between 283.15K and 323.15K fit in equation (8) to an accuracy of 0.01.

$$pK_3 = \frac{2397.4}{T} + 4.2364 - 2.6061\times10^{-2}T + 8.3834\times10^{-5}T^2 \quad \dots (8)$$

The values of thermodynamic quantities such as ΔG_3°, ΔH_3°, ΔS_3° and ΔCp_3° accompanying the dissociation of 1 mole of HPO_4^{2-} were computed statistically from equation (8). These values are recorded in Table 12.

TABLE 12—THERMODYNAMIC PARAMETERS OF $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ AT DIFFERENT TEMPERATURES

Temp/K	ΔH_3°/J mol^{-1}	ΔG_3°/J mol^{-1}	ΔS_3°/J mol^{-1} K^{-1}	ΔCp_3°/J mol^{-1} K^{-1}
283.15	13030	65295	−185	−490
288.15	10528	66240	−193	−512
293.15	7907	67229	−202	−535
298.15	5175	68264	−212	−559
303.15	2320	69347	−221	−583
308.15	−653	70475	−231	−607
313.15	−3749	71654	−241	−632
318.15	−6971	72883	−251	−657
323.15	−10323	74166	−261	−683

Our ΔH_3° value (1237 cal mol^{-1}) at 298.15K is somewhat lower than ΔH_3° values given by Pitzer[20] viz., 3500±500 cal mol^{-1} obtained calorimetrically and 5.8±0.8 k cal mol^{-1} (from K_3PO_4) and 4.8±0.3 k cal mol^{-1} (from Na_3PO_4) obtained from laser studies[10]. Our ΔH_3° value at 303.15K is also lower than ΔH_3° value given by Millero, Duer, Shepard and Chetirkin[21]. It is known that ΔH_3° found by e.m.f. and that found by direct calorimetric measurement are sometimes discrepant[22] and should be discrepant, because in calorimetric method we cannot be very sure of the extent of reaction.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1200-1203

Molecular Adsorption and Ion-exchange of Carboxylic Acids by Heteroionic Resins

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Manuscript received 17 August 1977, revised 11 August 1980, accepted 25 August 1980

Molecular adsorption and ion-exchange of carboxylic acids (C_2 to C_4) on heteroionic resins, $\left.\begin{matrix}H\\Na\end{matrix}\right\}$-*resin*, $\left.\begin{matrix}H\\K\end{matrix}\right\}$-*resin*, and $\left.\begin{matrix}Na\\K\end{matrix}\right\}$-*resin*, have been investigated. The cation-exchanger, Amberlite-IR-120, was saturated with two kinds of ions at three different mutual degrees of saturation. All the three acids are most strongly adsorbed by the potassium form; the order being R-K>R-H>R-Na. It is found that, the highest ion-exchange takes place from acetic acid and least from *n*-butyric acid. For all the three acids, Na^+ ion is more readily released than K^+ ion from their corresponding salt forms of the resin. The total ion-exchange from the heteroionic resin, $\left.\begin{matrix}Na\\K\end{matrix}\right\}$-resin, is greater than from purely sodium form or from purely potassium form of the resin. The ion-exchange curves show maxima between 25% and 50% of potassium ion in the heteroionic $\left.\begin{matrix}Na\\K\end{matrix}\right\}$-resin.

SYNTHETIC ion-exchange resins have the property of simultaneous ion-exchange and molecular adsorption, specially with weak electrolytes. Starobinets and Gleim[1], for the first time, investigated in some detail the differentiation between ion-exchange and molecular adsorption using carboxylic fatty acids with anion-exchange resins in chloride forms. In our previous communications[2,3], the results of study on ion-exchange and molecular adsorption with both cation-exchange as well as anion-exchange resins were reported. As electrolytes, some carboxylic acids and their different salts were used. The ion-exchange resins were also used in their different salt forms containing a single species of exchangeable ions.

The exchangeability of an ion from a heteroionic exchanger has been studied by many workers[4,5], using clay materials containing two different species of exchangeable ions. The work was extended by Pochhali[7] to synthetic ion-exchange resins, both cationic and anionic, in their heteroionic forms where two different species of exchangeable ions were introduced into the resins. Uptil now, no attempt has been made to investigate the simultaneous ion-exchange and molecular adsorption from weak electrolytes with heteroionic ion-exchanger containing two different species of exchangeable ions.

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In this paper, the results of the study on the molecular adsorption and the ion-exchange of carboxylic fatty acids by heteroionic cation-exchange resins, $\left.\begin{matrix}H\\Na\end{matrix}\right\}-R$, $\left.\begin{matrix}H\\K\end{matrix}\right\}-R$, $\left.\begin{matrix}Na\\K\end{matrix}\right\}-R$, with different degrees of saturation have been presented.

Experimental

Highly acidic cation-exchange resin, Amberlite-IR-120, a sulphonated polystyrene resin with 8% DVB, of the hydrogen form was saturated with two kinds of cations at three different degrees of saturation. The method of preparations of these kinds of resins has been described by Pochhali[7].

The hydrogen form of the resin with known moisture content and known exchange capacity (4.90 ± 0.04 meq/gm dry resin) was used for the preparation of the heteroionic resins.

Acetic, propionic and *n*-butyric acids of "AnalaR grades" were used for the investigations.

The experiments were done at room temperatures ($30^\circ \pm 2^\circ$). Weighed amounts (about 1 gm) of the air-dried resin of known moisture content were

TABLE 1

H / Na }—Resin

Acids		Degree of saturation in percentage of total cations in the resin				
		H : 100 Na : 0	H : 78.5 Na : 21.5	H : 57 Na : 43	H : 35.5 Na : 64.5	H : 0 Na : 100
Acetic :	Adsorption	0.230	0.216	0.190	0.170	0.142
	Exchange	0	0.067	0.119	0.184	0.300
Propionic :	Adsorption	0.240	0.246	0.240	0.250	0.240
	Exchange	0	0.059	0.101	0.156	0.280
n-butyric :	Adsorption	0.295	0.286	0.287	0.295	0.274
	Exchange	0	0.048	0.098	0.148	0.294

Both adsorption and exchange values are given in meq/gm. dry resin.

TABLE 2

H / K }—Resin

Acids		Degree of saturation in percentage of total cations in the resin				
		H : 100 K : 0	H : 76.3 K : 23.7	H : 51.5 K : 48.5	H : 27.6 K : 72.4	H : 0 K : 100
Acetic	Adsorption	0.230	0.245	0.280	0.270	0.280
	Exchange	0	0.022	0.086	0.209	0.288
Propionic	Adsorption	0.240	0.273	0.295	0.290	0.308
	Exchange	0	0.021	0.068	0.185	0.244
n-butyric	Adsorption	0.295	0.330	0.370	0.372	0.392
	Exchange	0	0.015	0.068	0.162	0.232

Both adsorption and exchange values are given in meq/gm. dry resin.

TABLE 3

Na / K }—Resin

Acids		Degree of saturation in percentage of total cations in the resin				
		Na : 0 K : 100	Na : 25 K : 75	Na : 50 K : 50	Na : 75 K : 25	Na : 100 K : 0
Acetic :	Na^+ exchange	0	0.083	0.250	0.334	0.300
	K^+ exchange	0.288	0.284	0.220	0.120	0
	Total exchange	0.288	0.367	0.470	0.454	0.300
	Adsorption	0.280	0.236	0.200	0.170	0.142
Propionic	Na^+ exchange	0	0.079	0.164	0.264	0.280
	K^+ exchange	0.244	0.248	0.202	0.102	0
	Total exchange	0.244	0.327	0.366	0.366	0.280
	Adsorption	0.308	0.290	0.278	0.262	0.240
n-butyric :	Na^+ exchange	0	0.078	0.176	0.254	0.294
	K^+ exchange	0.232	0.260	0.176	0.087	0
	Total exchange	0.232	0.338	0.352	0.341	0.294
	Adsorption	0.392	0.366	0.330	0.304	0.274

Both adsorption and exchange values are given in meq/gm. dry resin.

equilibrated with 50 ml of acid solutions of known concentration. After equilibrium the clear solutions were analysed for estimation of ions (i.e., Na^+ and K^+) and the acids in the equilibrium solutions.

The initial and equilibrium concentrations of the acids were found out by alkalimetric titrations with standard sodium hydroxide solutions using phenolphthalein indicator. The concentrations of Na^+ and K^+ ions in equilibrium solutions were found out by means of a Flame Photometer[8] ("EEL"), using appropriate filters for sodium and potassium.

Results and Discussion

With all the heteroionic resins for each degree of saturation, molecular adsorption and ion-exchange

(both in meq/gm dry resin) of the three carboxylic acids, acetic, propionic and *n*-butyric were measured at different equilibrium concentrations. These values were plotted against equilibrium concentrations of the acids. To study the variation of adsorption and ion-exchange with degree of saturation of the heteroionic resins, some particular equilibrium concentration for the acids was chosen. As most of the experiments were performed with the equilibrium concentrations ranging from 0 to 1.0 eqv/litre, the results are taken conveniently at equilibrium concentration of 0.5 eqv/litre. For this equilibrium concentration, molecular adsorption and ion-exchange of the acids were computed from the corresponding graphs. The results are tabulated in Tables 1 to 3 and presented graphically in Figures 1, 2, 3 respectively.

Comparing the adsorption of the acids on the three homoionic resins, it is found that all the three acids are most strongly adsorbed by the potassium form, the order being R – K > R – H > R – Na (Tables 1 and 2). Also it is found from Table 3, that, for all the three acids, Na^+ ion is more readily released than K^+ ion from their corresponding salt forms of the resin. This shows that K^+ ion is more strongly held than Na^+ ion by the resin. This indicates, that more strongly a counter-ion is held by the resin, stronger is the adsorption of the acids by that form of the resin.

Regarding the adsorption behaviour of the heteroionic resin, it is observed that, $\left.\begin{matrix}Na\\K\end{matrix}\right\}$ – resin behaves quite differently from $\left.\begin{matrix}H\\Na\end{matrix}\right\}$ – resin and $\left.\begin{matrix}H\\K\end{matrix}\right\}$ – resin. As has been mentioned above, that, for all the three acids, the adsorption is higher by the pure potassium form than the pure sodium form of the resin, the adsorption of the acids (as found from Fig. 3) increases almost linearly with increase in percentage of K^+ ion in the heteroionic $\left.\begin{matrix}Na\\K\end{matrix}\right\}$ – resin. But it is not so for $\left.\begin{matrix}H\\Na\end{matrix}\right\}$ – resin and $\left.\begin{matrix}H\\K\end{matrix}\right\}$ – resin. It is only in case of acetic acid with $\left.\begin{matrix}H\\Na\end{matrix}\right\}$ – resin, the adsorption decreases regularly with increase in percentage of Na^+ ion in the resin (Fig. 1). But in other cases, no regularity is found in the variation of adsorption with the degree of saturation of exchangeable ions. With $\left.\begin{matrix}H\\K\end{matrix}\right\}$ – resin, the adsorption of all the three acids (acetic, propionic, *n*-butyric), at first increases regularly from pure R-H upto about 50% of K^+ ion, afterwards adsorption has no tendency to increase, rather decreases, specially for acetic and propionic acids (Fig. 2). Similarly with $\left.\begin{matrix}H\\Na\end{matrix}\right\}$ – resin, the adsorption of propionic and *n*-butyric acids, at first increases with the percentage of H^+ ion in the resin, and then with further increase in the percentage of H^+ ion, there is a tendency to decrease (Fig. 1).

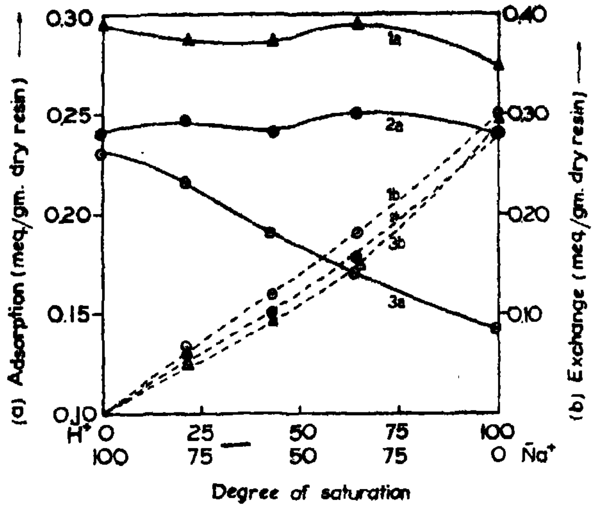


Fig. 1. $\left.\begin{matrix}H\\Na\end{matrix}\right\}$R + Carboxylic acid
(a) Adsorption (b) Exchange
1. Acetic (○) 2. Propionic (●) 3. *n*-butyric (▲)

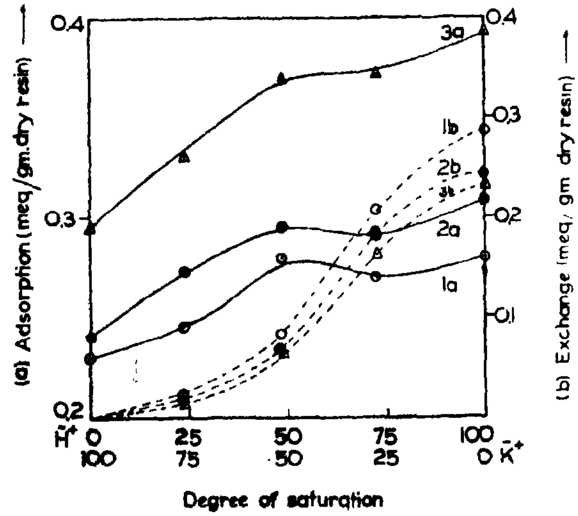


Fig. 2. $\left.\begin{matrix}H\\K\end{matrix}\right\}$R Carboxylic acid
(a) Adsorption (b) Exchange
1. Acetic (○) 2. Propionic (●) 3. *n*-butyric (▲)

It is found from Figures 1, 2, 3 that, in all the heteroionic resins the highest ion-exchange takes place from acetic acid, then from propionic acid and least from *n*-butyric acid. Considering the dissociation constants[6] of the acids, the position of *n*-butyric acid should have been between acetic and propionic acids. Here, the greater chainlength of

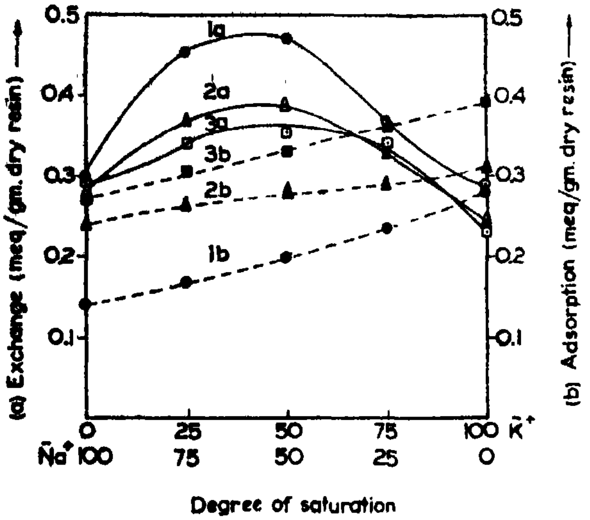


Fig. 3. $\left.\begin{matrix}Na\\K\end{matrix}\right\}$R + Carboxylic acid
(a) Total Ion-exchange, (b) Adsorption
1. Acetic (○,●) 2. Propionic (△,▲)
3. *n*-butyric (▣,■)

n-butyric acid masks the effect of dissociation constant and so ion-exchange is least in its case. In the cases of $\left.\begin{matrix}H\\Na\end{matrix}\right\}$ – resin and $\left.\begin{matrix}H\\K\end{matrix}\right\}$ – resin, as is expected, the ion-exchange increases with the degree of saturation with respect to the exchangeable ions in the resins (Figures 1 and 2). But $\left.\begin{matrix}Na\\K\end{matrix}\right\}$ – resin shows an interesting behaviour regarding the total ion-exchange (Fig. 3). The total ion-exchange from the heteroionic resin is greater than from purely sodium form or from purely potassium form. The ion-exchange curves show maxima and it is found that the maxima lie between 25% and 50% of potassium ion in the heteroionic resins for all the three acids.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1204-1207

Viscosity B-Coefficient of Some Amino Acids in Water

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Manuscript received 15 November 1978, revised 7 April 1980, accepted 25 August 1980

The viscosity B-coefficient of polyamino acids like DL-aspartic acid, DL-glutamic acid, L-histidine and L-arginine have been determined in aqueous solutions. The reported results indicate that the B values increase with the rise of temperature for aspartic and glutamic acids as compared to decrease observed for histidine and arginine ; a novelty explained in terms of protic and aprotic i.e., structure breaking and making behaviour of these amino acids in water or a sort of proton transfer reaction occurring in such system.

THE proteins are high polyamides derived from monomers of α-amino carboxylic acids and are the principal building materials of skin, muscle, nerves, blood, enzymes, antibodies, hormones etc. ; whereas the function of water is to maintain equilibrium in living system, by way of some unknown reversible biological processes. The imbalances produced in either of one beyond the reversibility of the process results in disorderness of the system and may cause serious hazards. Therefore, the role of a particular amino acid in water and its mechanism to control the functioning of the system is of utmost importance.

Thus, in view of the recent interest on account of their active role in biological processes, it would be desirable to study the mode of interaction, association and protonation of these amino acids in aqueous solutions. The present investigations are undertaken to determine coefficient B of Jones-Dole[1] viscosity equation, namely

$$\eta = \eta_o(1 + A\sqrt{C} + BC) \quad \ldots (1)$$

for aspartic, glutamic, histidine and arginine in water at different temperatures to study proton transfer properties as well as to elaborate molecular processes occurring in such systems.

Experimental

DL-aspartic acid (99%) obtained from BDH (Biochemical) Chemicals Ltd., Poole, England and DL-glutamic acid, L-arginine and L-histidine CHR puriss (>99%) purchased from Fluka A. G. Buchs. S. G., Switzerland were used after drying in a vacuum desiccator.

Solutions were prepared on molar basis in conductivity water and were corrected for the changes in volume at other temperatures.

Density and viscosity measurements were carried out in a Toshniwal make Constant Temperature Bath maintained within a maximum temperature fluctuation of $\pm 0.02°$. Density was determined with the help of a dilatometer and an Ubbelohde viscometer with a flow time of about 500 sec. for water was employed for measuring viscosity as described earlier[2,3].

The viscosity was calculated with the help of usual relation, namely :

$$\eta = \frac{d}{d_o} \times \frac{t}{t_o} \times \eta_o \quad \ldots (2)$$

From the viscosity data, the factors $\eta_{sp}/\sqrt{C}$ $\left(\eta_{sp} = \frac{\eta - \eta_o}{\eta_o}\right)$ were obtained for different solutions at various temperatures.

Results

The density and viscosity of DL-aspartic acid, DL-glutamic acid, L-histidine and L-arginine in water determined at different temperatures and concentrations are summarised alongwith $\eta_{sp}/\sqrt{C}$ values in Tables 1,2,3 and 4 respectively. The factor $\eta_{sp}/\sqrt{C}$ was plotted against $\sqrt{C}$ at different temperatures. The plots are almost linear, the slopes of which give the values of B and are given in Table 5 ; whereas the ordinate intercepts give coefficient A, representing contribution from interionic forces.

The coefficient A (for DL-aspartic : 0.006, DL-glutamic : 0.009, L-histidine : 0.008 and L-arginine : 0.014 at 25°) is found to be almost independent of temperature as well as 4-5% that of B values and therefore appears to be insignificant for detailed discussion.

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Table 1—Density, Viscosity and $\eta_{sp}/\sqrt{C}$ Values of DL-Aspartic Acid in Water at Different Temperatures and Concentrations

Conc. $C \times 10^3$ g. mole/lit	Density g/ml	Viscosity CP	$\eta_{sp}/\sqrt{C}$ $\left(\eta_{sp}=\frac{\eta-\eta_0}{\eta_0}\right)$
	25°C		
0.00	0.9970	0.894	...
0.25	0.9971	0.894	0.014
1.00	0.9973	0.895	0.021
2.50	0.9980	0.897	0.026
5.00	0.9991	0.901	0.036
10.00	1.0016	0.907	0.048
	30°C		
0.00	0.9956	0.801	...
0.25	0.9957	0.801	0.018
1.00	0.9960	0.803	0.026
2.50	0.9970	0.805	0.035
5.00	0.9979	0.809	0.046
10.00	1.0008	0.815	0.057
	35°C		
0.00	0.9940	0.722	...
0.25	0.9942	0.723	0.025
1.00	0.9944	0.725	0.036
2.50	0.9954	0.727	0.043
5.00	0.9974	0.731	0.054
10.00	0.9984	0.739	0.071
	40°C		
0.00	0.9922	0.656	...
0.25	0.9926	0.657	0.030
1.00	0.9928	0.659	0.040
2.50	0.9936	0.662	0.053
5.00	0.9954	0.666	0.065
10.00	0.9974	0.673	0.081

Table 2—Density, Viscosity and $\eta_{sp}/\sqrt{C}$ Values of DL-Glutamic Acid in Water at Different Temperatures and Concentrations

Conc. $C \times 10^3$ g. mole/lit	Density g/ml	Viscosity CP	$\eta_{sp}=/\sqrt{C}$ $\left(\eta_{sp}=\frac{\eta-\eta_0}{\eta_0}\right)$
	25°C		
0.00	0.9970	0.894	...
0.25	0.9972	0.895	0.024
1.00	0.9982	0.897	0.040
2.50	0.9991	0.902	0.056
5.00	1.0000	0.909	0.078
10.00	1.0030	0.923	0.103
	30°C		
0.00	0.9956	0.801	...
0.25	0.9959	0.802	0.030
1.00	0.9966	0.804	0.046
2.50	0.9977	0.808	0.058
5.00	0.9982	0.815	0.081
10.00	1.0020	0.828	0.108
	35°C		
0.00	0.9940	0.722	...
0.25	0.9942	0.724	0.036
1.00	0.9951	0.726	0.049
2.50	0.9961	0.730	0.066
5.00	0.9968	0.736	0.086
10.00	1.0000	0.749	0.116
	40°C		
0.00	0.9922	0.656	...
0.25	0.9924	0.657	0.040
1.00	0.9933	0.659	0.058
2.50	0.9947	0.664	0.073
5.00	0.9954	0.670	0.093
10.00	0.9984	0.682	0.124

Table 3—Density, Viscosity and $\eta_{sp}/\sqrt{C}$ Values of L-Histidine in Water at Different Temperatures and Concentrations

Conc. $C \times 10^3$ g. mole/lit	Density g/ml	Viscosity CP	$\eta_{sp}/\sqrt{C}$ $\left(\eta_{sp}=\frac{\eta-\eta_0}{\eta_0}\right)$
	25°C		
0.00	0.9970	0.894	...
0.25	0.9972	0.895	0.030
1.00	0.9973	0.898	0.048
2.50	0.9982	0.904	0.071
5.00	0.9994	0.913	0.098
10.00	1.0030	0.932	0.134
	30°C		
0.00	0.9956	0.801	...
0.25	0.9957	0.802	0.025
1.00	0.9958	0.804	0.048
2.50	0.9970	0.809	0.068
5.00	0.9980	0.818	0.094
10.00	1.0010	0.833	0.128
	35°C		
0.00	0.9940	0.722	...
0.25	0.9942	0.723	0.022
1.00	0.9943	0.725	0.040
2.50	0.9953	0.730	0.064
5.00	0.9965	0.737	0.089
10.00	0.9997	0.751	0.124
	40°C		
0.00	0.9922	0.656	...
0.25	0.9924	0.657	0.021
1.00	0.9927	0.659	0.039
2.50	0.9936	0.662	0.059
5.00	0.9948	0.669	0.085
10.00	0.9978	0.680	0.118

Table 4—Density, Viscosity and $\eta_{sp}/\sqrt{C}$ Values of L-Arginine in Water at Different Temperatures and Concentrations

Conc. $C \times 10^3$ g. mole/lit	Density g/ml	Viscosity CP	$\eta_{sp}/\sqrt{C}$ $\left(\eta_{sp}=\frac{\eta-\eta_0}{\eta_0}\right)$
	25°C		
0.00	0.9970	0.894	...
0.25	0.9974	0.895	0.033
1.00	0.9976	0.898	0.048
2.50	0.9982	0.902	0.070
5.00	0.9996	0.913	0.098
10.00	1.0010	0.930	8.128
	30°C		
0.00	0.9956	0.801	...
0.25	0.9959	0.802	0.029
1.00	0.9961	0.803	0.045
2.50	0.9968	0.809	0.064
5.00	0.9981	0.817	0.092
10.00	0.9999	0.832	0.128
	35°C		
0.00	0.9940	0.722	...
0.25	0.9944	0.723	0.025
1.00	0.9947	0.725	0.042
2.50	0.9952	0.729	0.061
5.00	0.9966	0.736	0.086
10.00	0.9992	0.750	0.117
	40°C		
0.00	0.9922	0.656	...
0.25	0.9929	0.657	0.021
1.00	0.9932	0.659	0.039
2.50	0.9934	0.662	0.057
5.00	0.9951	0.668	0.088
10.00	0.9981	0.680	0.114

TABLE 5—VISCOSITY B-COEFFICIENT OF DL-ASPARTIC, DL-GLUTAMIC, L-HISTIDINE AND L-ARGININE IN WATER AT DIFFERENT TEMPERATURES

Temp. °C	DL-aspartic acid	DL-glutamic acid	L-histidine	L-arginine
25	0.18	0.29	0.39	0.36
30	0.16	0.31	0.38	0.34
35	0.17	0.32	0.37	0.33
40	0.19	0.33	0.35	0.32

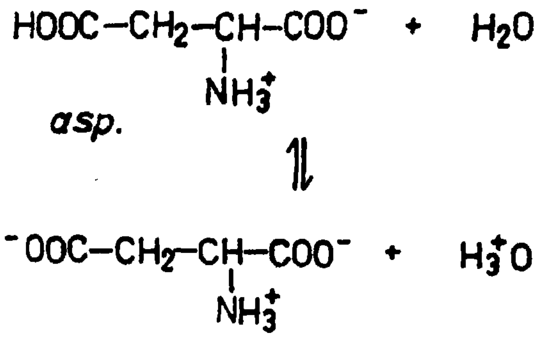
Discussion

It may be noted from Table 5 that dB/dT is positive for acidic amino acids like aspartic and glutamic in contrast to negative for basic amino acids like histidine and arginine ; the result can be explained in terms of protic and aprotic behaviour *i.e*, structure breaking and making feature of these polyamino acids in water following the arguments of others[4,5,6,7,8].

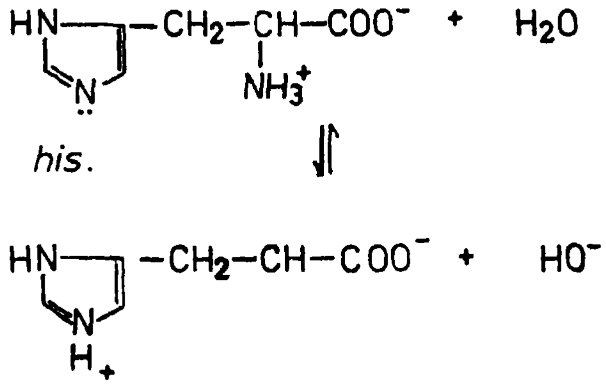
Further, it may be pointed out that the existence of free carboxylic group in acidic amino acids capable of yielding proton in solution which can be easily solvated to give H_3O^+ ion *i.e.*, resulting in protonation of water or a sort of disordering on account of the breaking of hydrogen bonded structure of water molecules, which obviously increases with the rise of temperature. Whereas in case of basic amino acids the free amino groups are responsible for the aprotic behaviour and can easily cause deprotonation of water molecules *i.e.*, long range ordering or a sort of enforcement of hydrogen bonded structure around these amino acids and therefore also accounts for the decrease in B values at higher temperatures.

The α-amino acids exist as zwitter ion in solution and their dissociation constants aspartic : 6.45×10^{-3} and glutamic : 8.3×10^{-3} have been reported, indicating the presence of free carboxylic group enabling them to enter into protonation or deprotonation processes and can be expressed by the following mechanism :

(a) *Protonation of water :*



(b) *Deprotonation of water :*



An attempt has been made to corroborate and interpret these results in terms of thermodynamic parameter entropy which is defined as a measure of randomness *i.e.*, the decrease in entropy means ordering or structure making while an increase indicates disordering or structure breaking of the system.

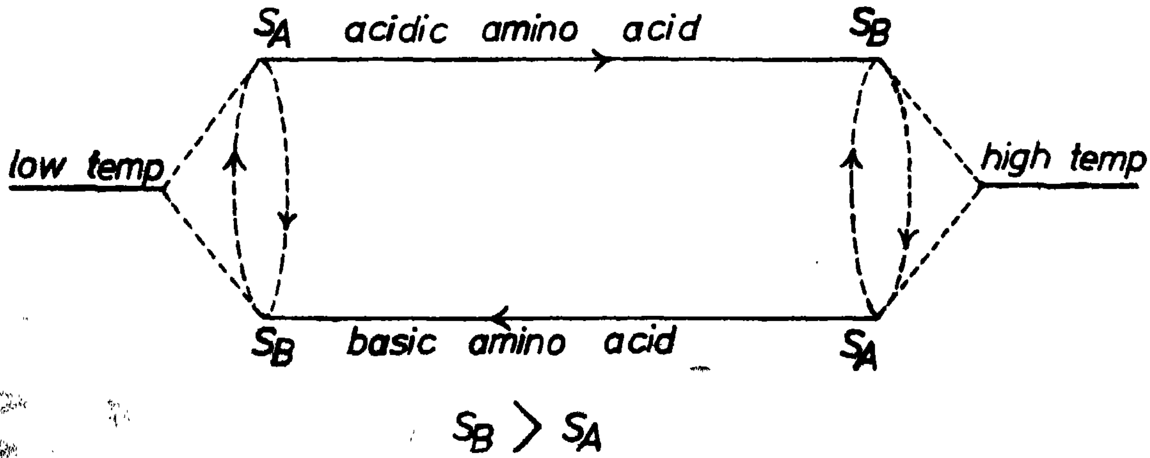


Fig. 1. Hypothetical representation of Biological Process to occur in presence of amino acids.

Thus from above considerations it can be fairly demonstrated that the system attains higher entropy state for acidic amino acids as compared to lower entropy state for basic amino acids with rise of temperature and on account of the difference in entropy states a biological process to occur.

Finally, it may be concluded in general that the protons or "cations" are structure breakers as compared to structure promotion feature of "anions" in aqueous solutions and causes the biological process to occur in presence of acidic or basic amino acids with the rise or fall of temperature as shown in Fig. 1.

Acknowledgement

Mr. O. P. Awasthi is grateful to University Grants Commission for awarding Teachers-Fellowship under Faculty Improvement Programme and to Dr. Tewarson, Principal, Lucknow Christian College for granting study leave. Thanks are also due to Prof. Ram Gopal for making us available polyamino acids.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1208-1212

Viscosity Variation with Composition : An Explanation in Terms of Various Solution Parameters

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Manuscript received 15 March 1980, revised 6 September 1980, accepted 9 September, 1980

The relative viscosities of naphthalene, durene, fluoranthene, fluorene, 2 : 3-dimethylnaphthalene, 2 : 6-dimethylnaphthalene and hexamethylbenzene have been measured in several solvents, namely toluene, *o*-xylene, *p*-xylene, *m*-xylene, mesitylene and heptane in the low concentration range of the solutes at 35°. It is noticed that the viscosity function, F decreases in the same order as the experimental slope, $S_0 = d\eta_{rel}/dX_2$.

NUMEROUS attempts[1] have been made over several decades to arrive at a correct formulation for the variation of viscosity of liquid mixtures as a function of composition. These attempts have been only partially successful. In the case of electrolyte solutions, however, Jones-Dole equation[2] has gained wide acceptance, especially because the parameters in the Jones-Dole equation are useful in obtaining an idea about ion-ion and ion-solvent interaction. Unfortunately it has not proved successful till now to interprete variation of viscosity of non-electrolyte liquid mixtures in a similar fashion and enable us to get information about solute-solute or solute-solvent interaction.

In the present article, we shall endeavour to show that the viscosity equation for liquid mixtures, proposed by Irving and Smith[3,4] provides us with an interpretation of viscosity variation in terms of solution parameters. Irving and Smith[3] extended Eyring theory of viscosity[5] to regular solutions and wrote for the relative viscosity, η_{rel} the following expression,

$$\eta_{rel} = \frac{\eta_s}{\eta} = \frac{V_1^o}{V_s} \exp\left[(\Delta E_s^v - \Delta E_1^v)/ART\right] \quad \ldots (1)$$

In equation (1) η_s is the absolute viscosity of the solution, η is the viscosity of the pure solvent, ΔE_s^v and ΔE_1^v are the molar energies of vaporisation of the solution and of the solvent respectively ; V_s and V_1^o are the molar volumes respectively of the solution and of the pure solvent, and A is a constant whose value is approximately 2.5. Now the energy of vaporisation of the solution, ΔE_s^v is related to the energy change ΔE^M on mixing by the relation,

$$\Delta E_s^v = X_1 \Delta E_1^v + X_2 \Delta E_2^v - \Delta E^M \quad (2)$$

at mole fraction X_1 and X_2 in respect of solvent and solute respectively, ΔE_1^v and ΔE_2^v are the molar energy of vaporisation of solvent and solute respectively. Following Scatchard[6], Irving and Smith[3] employed

$$\Delta E^M = (\delta_1 - \delta_2)^2 X_2 \bar{V}_2$$

in very dilute solutions ; δ_1 and δ_2 are the solubility parameters[7] of solvent and solute and $\bar{V}_2$ is the partial molal volume of the solute. Noting that in very dilute solutions $V_1^o/V_s \simeq 1$, Irving and Smith[3] finally obtained

$$\eta_{rel} = 1 + S_0 X_2 \quad \ldots (3)$$

In equation (3) S_0 represents the rate of variation of η_{rel} with mole fraction of the solute, $d\eta_{rel}/dX_2$ and is given by

$$S_0 = \{-\delta_1^2(V_1^o + \bar{V}_2) + 2\bar{V}_2\delta_1\delta_2\}/ART \quad \ldots (4)$$

for solutions having $\bar{V}_1 \simeq V_1^o$.

Let us now study the consequences flowing from Irving and Smith equation (3). We define the viscosity function, F as follows :

$$F = \bar{V}_2\left(\frac{2\delta_2}{\delta_1} - 1\right) \quad \ldots (5)$$

With the aid of the viscosity function, F we can rewrite expression (4) for S_0,

$$S_0 = \{\delta_1^2(F - V_1^o)\}/ART \quad \ldots (6)$$

It follows that the value of S_0 will be positive only if F is positive (i.e. $2\delta_2 > \delta_1$) and greater than V_1^o.

It is seen that the solubility parameters together with the partial molar volumes of solvent and solute determine the variation of viscosity with composition. That this is borne out by experimental results is described below with reference to viscosity of solutions of solutes. ortho-terphenyl, 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, fluoranthene,

fluorene, hexamethylbenzene, naphthalene and durene in several solvents, namely, toluene, xylenes, mesitylene and *n*-heptane.

Experimental

Materials : The solvents used are : mesitylene (Merck, Germany), *n*-heptane (BDH, England), *o*-xylene (BDH, England) *p*- and *m*-xylene (E. Merck, Germany), toluene (International Chemical Industry, Calcutta). *n*-Hetane was fractionally distilled. Toluene was purified by shaking several times with concentrated H_2SO_4. It was then shaken first with water, then sodium carbonate solution and again with water and finally dried over anhydrous calcium chloride and fractionally distilled. All the solvents were freshly distilled before use. Naphthalene (E. M., Germany), Durene (KL, England), 2 : 3-dimethylnaphthalene (KL, England), 2 : 6-dimethylnaphthalene (KL, England), *o*-terphenyl (KL, England), fluoranthene (KL, England), fluorene (KL, England) were the best quality available and recrystallised from appropriate solvents.

Measurement of density and viscosity :

The densities of the pure solvents and of solutions were measured by a bicapillary pycnometer[8]. From the measured densities d, the molar volumes were calculated using the relation,

$$V_m = (X_1M_1 + X_2M_2)/d$$

where X_1, X_2, M_1 and M_2 are the mole fractions and molecular weights of solvent and solute respectively. The plot of V_m against X_2 is linear in accordance with the equation[8],

$$V_m = V_1^o + (\bar{V}_2 - V_1^o)X_2 \qquad \dots (7)$$

With V_1^o for the pure solvent known, it is now easy to determine $\bar{V}_2$ from the slope of the plot of V_m against X_2.

The relative viscosities of the solutions were measured in an Ubbelohde suspended level viscometer having viscometer constants, $A = 2.7321 \times 10^{-3}$ stokes/sec and $B = 1.3378 \times 10^{-2}$ stokes-sec. Kinetic energy correction was however negligible and the relative viscosity was determined from the relation, $\eta_{rel} = \frac{d_1t_1}{d_0t_0}$, where d_0, t_0 and d_1, t_1 are density and time of flow of pure solvent and solution respectively. Flow times were measured with a stopwatch reading upto $\frac{1}{10}$th of a second. All measurements of density and of flow times were done in a thermostated bath at 35±0.05°.

Results and Discussion

Table 1 gives the experimental results of viscosity measurements of solutions of the hydrocarbons in various solvents. The plot of η_{rel} vs X_2, mole fraction of solute is linear for all the solutes in these solvents. Figure 1 is a typical linear plot of η_{rel} vs X_2 of fluorene in the solvents in the low concentration range used in the present investigation. The experimental values of the slope, S_0 of the η_{rel} vs X_2 plot are also given in Table 4. The plots of V_m vs mole fraction of all the solutes, X_2 in these solvents

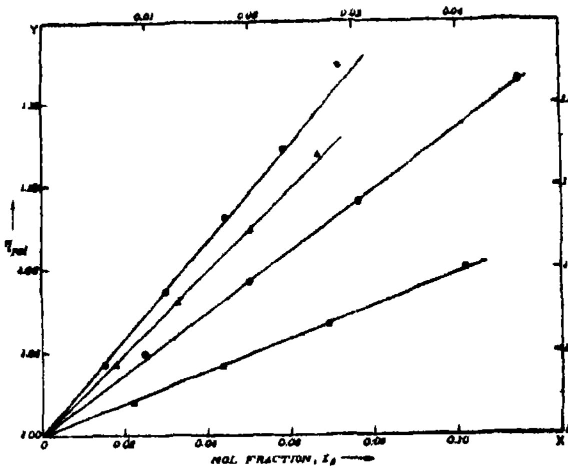


Fig. 1. Plot of η_{rel} vs mole fraction, X_2 of Fluorene in several solvents

△-*p*-xylene, O-toluene: Left hand Y axis and lower X axis

●-mesitylene ; Right hand Y axis and upper X axis

□-*o*-xylene ; Left hand Y axis and upper X axis

TABLE 1—RELATIVE VISCOSITIES OF HYDROCARBONS IN SOLVENTS AT 35±0.05°

Solvent	Mole fraction of solute X_2	η_{rel}	Solvent	Mole fraction of solute X_2	η_{rel}
		Naphthalene			
o-xylene	0.0225	1.0257	*m*-xylene	0.0489	1.0510
	0.0440	1.0461		0.0648	1.0774
	0.0644	1.0657		0.0888	1.1129
	0.0843	1.0967		0.1085	1.1800
p-xylene	0.0225	1.0286	toluene	0.0070	1.0087
	0.0464	1.0508		0.0128	1.0150
	0.0681	1.0766		0.0613	1.0779
	0.0888	1.1052			
n-heptane	0.0679	1.0672			
	0.1028	1.1101			
	0.1273	1.1399			
		2 : 3-dimethylnaphthalene			
o-xylene	0.0185	1.0248	*m*-xylene	0.0187	1.0300
	0.0329	1.0447		0.0380	1.0580
	0.0466	1.0650		0.0503	1.0777
	0.0608	1.0858		0.0669	1.1049
p-xylene	0.0190	1.0288	mesitylene	0.0210	1.0316
	0.0446	1.0638		0.0410	1.0606
	0.0569	1.0884		0.0582	1.0829
	0.0741	1.1067		0.0715	1.1079

(Table 1 Contd.)

Solvent	Mole fraction of solute X_2	η_{rel}	Solvent	Mole fraction of solute X_2	η_{rel}
		2 : 6-dimethylnaphthalene			
o-xylene	0.0165	1.0257	*m*-xylene	0.0165	1.0315
	0.0364	1.0491		0.0364	1.0593
	0.0567	1.0766		0.0567	1.0838
	0.0744	1.1007		0.0784	1.1186
	0.0928	1.1268			
p-xylene	0.0196	1.0258	mesitylene	0.0209	1.0242
	0.0365	1.0516		0.0433	1.0509
	0.0600	1.0824		0.0556	1.0682
	0.0784	1.1084		0.0674	1.0872
	0.0961	1.1345			
toluene	0.0162	1.0260			
	0.0317	1.0511			
	0.0468	1.0768			
	0.0608	1.1004			
	0.0757	1.1266			
		o-terphenyl			
o-xylene	0.0064	1.0189	*m*-xylene	0.0064	1.0255
	0.0128	1.0497		0.0127	1.0486
	0.0211	1.0786		0.0189	1.0751
	0.0250	1.0955		0.0250	1.0975
				0.0341	1.1333
p-xylene	0.0064	1.0233	mesitylene	0.0072	1.0201
	0.0134	1.0483		0.0143	1.0495
	0.0199	1.0737		0.0213	1.0689
	0.0264	1.1002		0.0282	1.1010
	0.0341	1.1292		0.0336	1.1158
		Durene			
m-xylene	0.0322	1.0191	*p*-xylene	0.0399	1.0188
	0.0587	1.0353		0.0811	1.0497
	0.0873	1.0510		0.1114	1.0629
	0.1203	1.0701		0.1467	1.0743
toluene	0.0176	1.0092	*n*-heptane	0.0335	1.0271
	0.0348	1.0183		0.0650	1.0538
	0.0673	1.0406		0.1105	1.0921
		Hexamethylbenzene			
o-xylene	0.0184	1.0258	*m*-xylene	0.0179	1.0302
	0.0288	1.0428		0.0319	1.0545
	0.0426	1.0657		0.0489	1.0751
	0.0551	1.0850		0.0647	1.1003
mesitylene	0.0203	1.0277			
	0.0359	1.0466			
	0.0509	1.0719			
	0.0666	1.0965			
		Fluoranthene			
o-xylene	0.0072	1.0223	*p*-xylene	0.0144	1.0101
	0.0144	1.0444		0.0214	1.0611
	0.0283	1.0887		0.0283	1.0821
	0.0419	1.1389		0.0391	1.1207
	0.0551	1.1780		0.0525	1.1566
mesitylene	0.0082	1.0226	toluene	0.0125	1.0422
	0.0162	1.0450		0.0230	1.0755
	0.0257	1 0721		0.0318	1.1068
	0.0350	1.1005		0.0414	1.1409
	0.0472	1.1886		0.0500	1.1747
		Fluorene			
o-xylene	0.0088	1.0160	*p*-xylene	0.0177	1.0388
	0.0175	1.0336		0.0327	1.0687
	0.0276	1.0582		0.0502	1.0985
	0.0408	1.0807		0.0666	1.1349
mesitylene	0.0099	1.0196	toluene	0.0151	1.0341
	0.0208	1.0869		0.0298	1.0695
	0.0311	1.0561		0.0441	1.1047
	0.0460	1.0852		0.0581	1.1380
	0.0604	1.1182		0.0717	1.1775

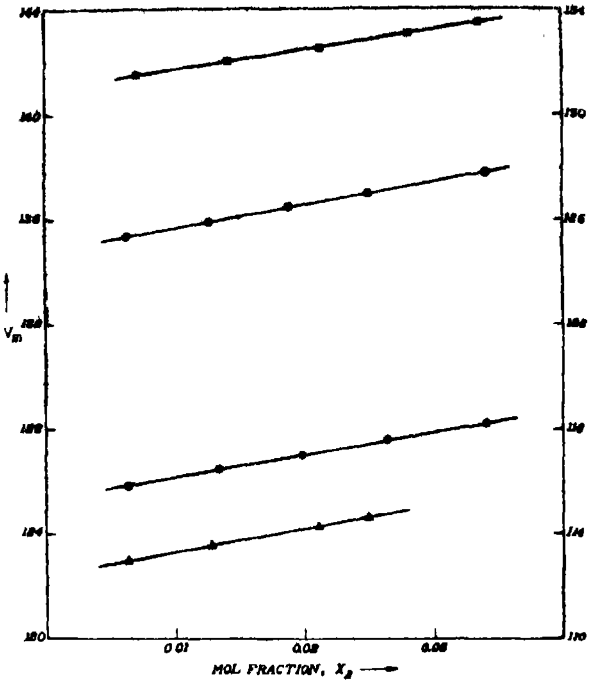


Fig. 2. Plot of V_m vs mole fraction, X_2 of *o*-terphenyl in several solvents. O-*p*-xylene, Δ-*o*-xylene and □-mesitylene ; Left hand Y axis
●-*m*-xylene, Right hand Y axis

are linear and a typical plot is shown in Fig. 2. The values of $\bar{V}_2$ as determined from the slope are given in Table 2 together with the values of V_1^o for the pure solvents.

To obtain the value of A in expression (6) for solvents, we employ the relation[8],

$$A = \frac{\Delta E_1^v}{\Delta G^*_{vis}} = \frac{\Delta H_1^v - RT}{\Delta G^*_{vis}}$$

From the published vapour pressure[1] of the solvents, we evaluated ΔH_1^v, enthalpy of vaporisation of solvents from the linear plot of log (vapour pressure) vs 1/T. With the help of Eyring equation for viscosity of pure solvent, η,

$$\eta = \frac{Nh}{V_1^o} \exp\left(\Delta G^*_{vis}/RT\right) \qquad \ldots (8)$$

it is possible to obtain the value of ΔG^*_{vis}, free activation energy of viscous flow for a solvent with known viscosity at T°K. In eq. (8) R, N and h are molar gas constant, Avogadro's number and Planck's constant respectively. The viscosities of the solvents at 35° were used for evaluating ΔG^*_{vis} given in Table 3. With the values of ΔE_1^v and ΔG^*_{vis} thus determined, we calculated the value of A for the solvents and these are given in Table 3. The values of the solubility parameter δ_1 for

TABLE 2—VALUES OF $\overline{V}_2$, V_1^0, δ_1 AND δ_2 AT 35±0.05°C

Solvent	Naphthalene $\overline{V}_2$(cc mole^{-1})	Naphthalene δ_2	Durene $\overline{V}_2$(cc mole^{-1})	Durene δ_2	2 : 3-dimethylnaphthalene $\overline{V}_2$(cc mole^{-1})	2 : 3-dimethylnaphthalene δ_2	2 : 6-dimethylnaphthalene $\overline{V}_2$(cc mole^{-1})	2 : 6-dimethylnaphthalene δ_2	Hexamethylbenzene $\overline{V}_2$(cc mole^{-1})	Hexamethylbenzene δ_2
o-xylene	124.89	9.70	—	—	155.46	8.95	159.18	8.79	175.62	8.497
m-xylene	124.49	9.78	154.10	8.40	155.05	8.93	157.69	8.80	175.40	8.47
p-xylene	125.03	9.60	152.72	8.38	156.01	8.82	158.42	8.69	—	—
mesitylene	—	—	—	—	156.24	8.92	158.18	8.76	175.22	8.40
n-heptane	124.64	9.00	153.41	7.89	—	—	—	—	—	—
toluene	124.85	9.17	154.00	7.86	—	—	158.07	8.44	—	—
Mean :		9.44±0.33		8.13±0.30		8.90±0.06		8.696±0.15		8.45±0.05

Solvent	o-terphenyl $\overline{V}_2$(cc mole^{-1})	o-terphenyl δ_2	Fluoranthene $\overline{V}_2$(cc mole^{-1})	Fluoranthene δ_2	Fluorene $\overline{V}_2$(cc mole^{-1})	Fluorene δ_2	Solvents V_1^0(cc mole^{-1})	Solvents δ_1
o-xylene	215.88	8.83	172.12	9.58	154.20	9.33	122.18	8.96
m-xylene	213.36	8.79	—	—	—	—	124.49	8.75
p-xylene	213.60	8.76	171.398	9.32	152.95	9.26	125.08	8.70
mesitylene	213.19	8.26	171.25	9.04	153.06	9.15	140.96	8.76
n-heptane	—	—	—	—	—		149.03	7.40
toluene	—	—	172.92	9.04	152.64	9.04	107.93	8.86
Mean :		8.66±0.27		9.24±0.26		9.19±0.13		

solvents at 25° are already available in literature[7]. Assuming that ΔE_1^V is independent of temperature, the value of δ_1 at 35° was determined by multiplying its value at 25° with the ratio of partial molal volumes of the solvent at these two temperatures. The values of δ_1 at 35° are given in Table 2. We can now determine the solubility parameter of a solute hydrocarbon, if we substitute in eq. (4) the values of δ_1, V_1^0, $\overline{V}_2$, A and the experimental S_0 which are given in Tables 2, 3 and 4 respectively. We have thus determined δ_2 for the various solutes and these are given in Table 2 along with the mean over various solvents. We now calculate the viscosity function, $F=\overline{V}_2\left(\frac{2\delta_2}{\delta_1}-1\right)$ using the mean values of δ_2. The values of $\overline{V}_2$ and δ_1 necessary for the calculation are taken from Table 2. We observe

TABLE 3—VALUES OF $\Delta G^{\bullet}_{vis}$, ΔE_1^V AND A FOR PURE SOLVENTS AT 35±0.05°C

Solvents	ΔH_1^V (cal mole^{-1})	$\Delta E_1^V=\Delta H_1^V-RT$ (cal mole^{-1})	$\Delta G^{\bullet}_{vis}$ (cal mole^{-1})	A
o-xylene	10284	9672	3249	2.977
m-xylene	9776	9164	3112	2.945
p-xylene	9908	9296	3136	2.965
mesitylene	6358	5746	3267	1.759
n-heptane	8494	7882	2980	2.645
toluene	8764	8152	2991	2.725

TABLE 4—VALUES OF S_0 AND F FOR SOLUTES IN DIFFERENT SOLVENTS

Solvents	o-terphenyl >	Fluoranthene >	Fluorene >	Hexamethyl-benzene	> 2 : 3 DMN† >	2 : 6 DMN† >	Naphthalene >	Durene
o-xylene S_0 (Expt)	3.8461	3.2401	1.9624	1.5438	1.4461	1.3516	1.0803	–
F	190.15	183.07	162.12	155.63	153.55	149.94	134.36	
m-xylene S_0 (Expt)	3.8559	–	–	1.6842	1.5614	1.4921	1.1935	0.6038
F	197.56	–	–	163.37	160.54	155.89	140.13	128.74
p-xylene S_0 (Expt)	3.8257	2.9394	1.9697	–	1.4621	1.3647	1.0806	0.6818
F	200.15	192.87	170.18	–	163.36	158.42	142.27	129.20
n-heptane S_0 (Expt)	–	–	–	–	–	–	1.0000	0.8293
F	–	–	–	–	–	–	188.64	179.53
toluene S_0 (Expt)	–	3.3958	2.4024	–	–	1.6537	1.2162	0.5283
F	–	187.95	164.01	–	–	152.36	137.25	125.15
mesitylene S_0 (Expt)	3.40	2.9198	1.8276	1.4067*	1.50*	1.2192	–	–
F	196.93	190.23	168.08	162.83	161.41	156.01	–	–

† DMN : Dimethylnaphthalene.

* It is noted that for solutes hexamethylbenzene and 2 : 3-dimethylnaphthalene the order of S_0 is reversed in mesitylene.

that the viscosity function is always positive as it should be. Further, F decreases in the same order as experimental (mean) S_0 shown in Table 4 for the various solutes in the given solvents. Excepting for the solvent mesitylene, it is seen that the computed values of F decrease in the same order as the observed values of S_0, as it should. It is evident that the prediction that larger the value of the viscosity function, F, the greater will be the slope, S_0 of the plot of η_{rel} vs X_2 is generally fulfilled by the above experimental results. It is true that we should have made an independent determination of δ_2 for evaluating the viscosity function, F. In absence of any independent estimate of δ_2, we have taken values of δ_2 averaged over several solvents. In addition to the fact that Irving and Smith equation gives a new method for estimating solubility parameters, it is all the more important because it brings out clearly that it is the solubility parameters and partial molar volumes of solvent and solute that determine in a large measure the viscosity behaviour of non-electrolyte solutions.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1213-1215

Studies on Some Physical Properties of Sesame Oil in Mixed Solvents

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Manuscript received 21 August 1979, revised 23 July 1980, accepted 25 August 1980

The mutual solubility of sesame oil in ethanol by another solvent, *n*-hexane, cyclohexane or isopropanol was increased by increasing the temperature of the solution. Physical properties—density, viscosity, surface tension and refractive index of the solubilized solution of sesame oil in the mixed solvents have been studied at the temperature at which solution becomes clear.

THE mutual solubility of two normally immiscible liquids may increase by the addition of a third substance which acts at the interface of two immiscible liquids. This phenomenon, known as solubilization, depends on the nature of the solvent, chain length, temperature and presence of various additives. A solubilized product is clear because the particle size of the emulsion is so small that light is not refracted by the particles.

Sugiyama *et al*[1] used the highly concentrated solution of color-formers in mineral or vegetable oils and solubilized them by the addition of organic peroxides. Lubowe[2] solubilized the mixture of lower alcohols (1-3C atoms) and mineral, vegetable and animal oils by the addition of proportions of fatty alcohols having 10-24C atoms. Kharin, *et al*[3] studied density, refractive index, viscosity and surface tension of three component systems. Lazarev[4], studied the surface tension of an ideal ternary solution. Butler, *et al*[5] studied density, surface tension, viscosity, refractive index of ternary system Benzene-Cyclohexane Hexane.

Experimental

In the present work sesame oil has been employed to increase its solubility in ethanol using η-hexane, cyclohexane or isopropanol and studied the physical properties—density, viscosity, surface tension and refractive index of its solubilized solutions. The variation of these physical properties of solubilized solution of sesame oil in mixed solvents of ethanol with above mentioned solvents have been studied at the temperature at which solution becomes clear.

The general procedure adopted was to add, using a magnetic stirrer, appropriate amount of another solvent (η-hexane, cyclohexane or isopropanol) in the mixture of sesame oil in ethanol, but as another solvent is added in the mixture, turbidity appears which disappeared after increasing the temperature of the solution. At this temperature sesame oil is said to be solubilized in ethanol. The amount of ethanol and above mentioned solvents in each set of observation was fixed and that of sesame oil was varied. Thermostat was used to increase the temperature of the solution till a transparent one phase system is obtained and then studied the above mentioned physical properties of the transparent solution at this temperature. Ethanol used was of 98% purity. In each set solution was prepared by weight ranging from 2 gm to 10 gm of oil and the weight of ethanol and the other solvent was fixed 50 gm each. The weight fraction of sesame oil is calculated, at a temperature at which solution becomes clear.

In each set viscosity of the solubilized solution was determined by Ostwald viscometer and was calculated by the usual method. Surface tension of the solution was determined by double capillary rise method of Richards, Speyer and Carvar[6], with slight modification using the formula $\gamma_{solution} = KHd$, where $\gamma_{solution}$ = surface tension of solution, H = difference in height, d = density of the solution and K = apparatus constant. Difference in height was measured by cathetometer. Refractive index of the solution was measured by Abbe's refractometer. Observations were taken at the temperature at which solution become clear. The characteristics of the sesame oil used were :

At 30° sp. gravity 0.9134 gm/c. c., viscosity 42.1932 c. p., surface tension 24.3245 dynes/cm, refractive index 1.4702.

In tables 1-3, the data of the weight fraction of sesame oil, density, viscosity, surface tension and refractive index of the solubilized solution of sesame oil in above mentioned mixed solvents have been shown.

Discussion

The variation of the viscosity, surface tension and refractive index of the solubilized solution of

TABLE 1—SESAME OIL-ETHANOL-η-HEXANE

(Ethanol & n-hexane were taken 50 gm each at the temperature at which clear solution is obtained)

Weight fraction of sesame oil at the temperature at which clear solution is obtained	Temperature at which clear solution is obtained	Density of the solution in gm/c.c.	Viscosity of solution in c.p. $\eta_{solution}$	Surface tension of solution in dynes/cm $\gamma_{solution}$	Refractive index of the solution $\mu_{solution}$
24×10^{-3}	25°	0.7451	0.8261	27.9985	1.3750
48×10^{-3}	30°	0.7468	0.8399	21.1866	1.3780
70×10^{-3}	35°	0.7484	0.8699	17.8584	1.3810
91×10^{-3}	40°	0.7574	0.8815	15.8767	1.3844
112×10^{-3}	45°	0.7595	0.8980	14.9684	1.3870

TABLE 2—SESAME OIL-ETHANOL-CYCLOHEXANE

(Ethanol & Cyclohexane were taken 50 gm each at the temperature at which solution becomes clear)

Weight fraction of sesame oil at the temperature at which clear solution is obtained	Temperature at which clear solution is obtained	Density of solution in gm/c.c	Viscosity of solution in c.p. $\eta_{solution}$	Surface tension of solution in dynes/cm. $\gamma_{solution}$	Refractive index of the solution $\mu_{solution}$
23×10^{-3}	30°	0.7894	0.9092	21.2568	1.3900
45×10^{-3}	35°	0.7969	0.9362	16.0996	1.3930
66×10^{-3}	40°	0.7998	0.9582	13.6806	1.3960
79×10^{-3}	45°	0.8675	0.9762	12.0208	1.3990
94×10^{-3}	50°	0.8994	0.9820	11.7245	1.4020

TABLE 3—SESAME OIL-ETHANOL-ISOPROPANOL

(Ethanol & Isopropanol were taken 50 gm each at the temperature at which clear solution is obtained

Weight fraction of sesame oil at the temperature at which clear solution is obtained	Temperature at which clear solution is obtained	Density of solution in gm/c.c.	Viscosity of solution in c.p. $\eta_{solution}$	Surface tension of solution in dynes/cm $\gamma_{solution}$	Refractive index of the solution $\mu_{solution}$
22×10^{-3}	38°	0.8024	1.3293	24.8296	1.3800
44×10^{-3}	45°	0.7962	1.2872	27.4895	1.3830
66×10^{-3}	50°	0.7892	1.2462	29.7824	1.3860
88×10^{-3}	55°	0.7817	1.2281	31.8482	1.3910
110×10^{-3}	60°	0.7751	1.2162	33.6243	1.3970

sesame oil in mixed solvents (Ethanol with *n*-Hexane, Cyclohexane and Isopropanol) with the weight fraction of sesame oil at the temperature at which clear solution is obtained—is shown in Fig 1. Curves A, B, C show the variation of viscosity with the weight fraction of oil and Curves A′, B′, C′, the variation of surface tension with the weight fraction of oil when η-hexane, cyclohexane and isoproponal were used for increasing the solubility of sesame oil in ethanol respectively. These curves show that in the case of η-hexane and cyclohexane, viscosity of the solution increases while surface tension decreases with the weight fraction of oil but in the case of isopropanol viscosity decreases and surface tension increases. It may likely be due to the fact that isopropanol is more polar than η-hexane and cyclohexane. Curves A″, B″, C″ show the variation of refractive index with the weight fraction of oil. These curves show that in each case refractive index of the solution increases with the weight fraction of oil which indicates that refractive index is independent on the polarity of another solvent, The

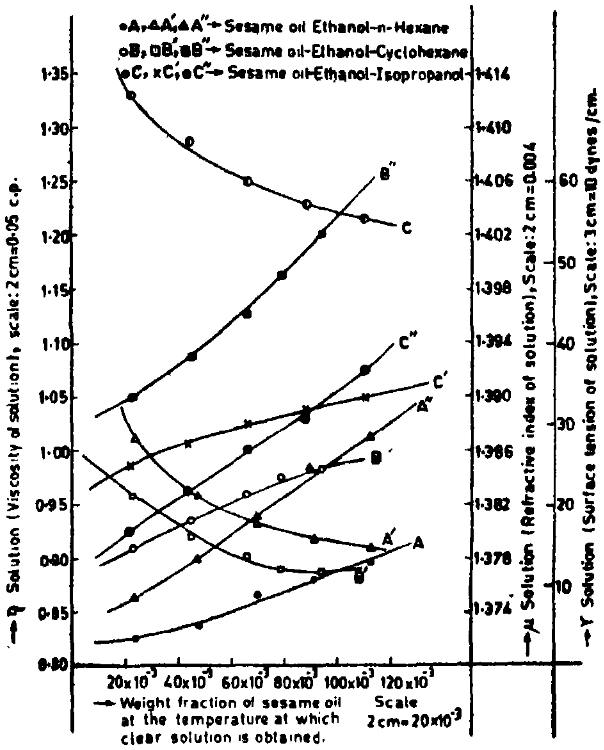


Fig. 1.

variation of the above mentioned physical properties with the temperature at which clear solution is obtained, is similar to the weight fraction effect.

Acknowledgement

The authors are thankful to the authorities of Meerut College, Meerut for providing necessary facilities. One of them (M. L) is thankful to C. S. I. R. New Delhi for financial assistance.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1216-1218

Ion-Solvent Interaction and Solvation Numbers of Alkali Metal Nitrates in Dimethyl Sulfoxide at 25°C

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Manuscript received 2 January 1979, revised 16 October 1979, accepted 25 August 1980

The Fuoss-Onsager-Skinner Conductance Equation has been used to analyse high precision conductance data of alkali metal nitrates in DMSO at 25°. The association constants calculated are in the order $NaNO_3 > KNO_3 > RbNO_3 > CsNO_3 > LiNO_3$. The sizes of the solvodynamic units have been estimated by the Nightingale method. Solvation numbers of the ions are Li^+ 4.3, Na^+ 3.2, K^+ 2.87, Rb^+ 2.75, Cs^+ 2.54 and NO_3^- 1.39. The solvated Li_s^+ has almost the same size as that of the Bu_4N^+ ion (tetrabutylammonium ion).

CONDUCTANCE measurements provide an insight into ion-ion and ion-solvent interactions in electrolyte solutions. Ramgopal and Jha[1] have determined the solvation numbers of some alkali metal ions from transport number measurements of KBr in DMSO and from the conductance data of alkali metal salts in DMSO reported in literature. High precision conductance data of alkali metal nitrates in non-aqueous solvents especially in DMSO are not available in literature. In this work the association constants, the extent of solvation and solvation numbers of the alkalimetal and nitrate ions have been determined from conductance data of high precision (±0.02%).

Experimental

DMSO (A.R. grade) was purified by vacuum fractionation[2] The middle fraction was repeatedly fractionated till the specific conductance of the final product was $2-3\times10^{-8}$ ohm^{-1} cm^{-1}. The purified solvent was stored in a dry box in an atmosphere of pure dry N_2. The water content determined by Karl Fischer titration was 0.001% by wt. The physical constants measured at 25° were : m.p., 18.55° ; d., 1.0958 g cm^{-3} ; sp. cond., $2-3\times10^{-8}$ ohm^{-1} cm^{-1} ; Diel. const., 46.6. The values reported in literature[3] are m.p., 18.55° ; d., 1.096 g cm^{-3} ; sp. cond.., 3×10^{-8} ohm^{-1} cm^{-1} ; Diel. const., 46.6.

The alkali metal nitrates (AnalaR) were purified by repeated recrystallisation from conductance water. They were all dried in vacuo at 120°. The purity was determined by gravimetric analysis of the metal content[4]. The purity in all cases was better than 99.98%.

The direct current technique developed by Gunning and Gordon[5] was employed for the conductance measurement. A modified Gordon cell in conjunction with the liquid junction probe chambers devised by Elias and Schiff[6] were used. A solution of 0.01 *N KCl in methanol* was used as the probe solution. The measurements were made during the winter season at night when the ambient temperature was well below 25°. The temperature regulation of the order 25.0±0.005 was obtained in a thermostatic bath which contained about 30 litres of light transformer oil. Thermo regulation was effected by a highly sensitive electronic relay. Details of the experimental procedure were as given by Unni *et al*[7].

Results and Discussion

The conductance data are given in Table 1.

The Fuoss-Onsager-Skinner conductance equation[8] has been used to analyse the data. Since the maximum concentration studied is only about 10^{-2} equiv. l^{-1}, γ is assumed to be unity and the equation suggested by the authors for dilute solutions has been used. The equation has the form

$$\Lambda = \Lambda_0 - Sc^{\frac{1}{2}} + E' c \ln (6E'_1 c) + Lc - A\Lambda_0 cf^2 \quad \dots (1)$$

where $A = K_A$. All the terms have been described by the authors of the equation. A function Λ' can be defined as

$$\begin{aligned}\Lambda' &= \Lambda + Sc^{\frac{1}{2}} - E' c \ln (6E_1' c)\\ &= \Lambda_0 + (L - Af^2\Lambda_0)c \end{aligned} \quad (2)$$

A plot of Λ' against c should be linear with slope $L - A\,\Lambda_0\,f^2$ and intercept Λ_0. An approximate initial value of Λ_0 obtained from a Shedlovsky plot was used to calculate the initial values of Λ'. Λ_0 and slopes were calculated by least mean square analysis. The refined values of Λ_0 were used to recalculate Λ'. The least mean square analysis

TABLE 1—EQUIVALENT CONDUCTANCES OF ALKALI METAL NITRATES IN DMSO AT 25°C AT DIFFERENT CONCENTRATIONS
(c in equiv. l^{-1} ; Λ in ohm^{-1} cm^{+2} $equiv.^{-1}$)

$LiNO_3$		$NaNO_3$		KNO_3		$RbNO_3$		$CsNO_3$	
$c \times 10^4$	Λ	$c \times 10^4$	Λ	$c \times 10^4$	Λ	$c \times 10^4$	Λ	$c \times 10^4$	Λ
4.687	37.130	6.289	39.106	4.508	40.122	5.500	40.861	5.001	41.044
17.212	36.099	9.734	38.732	8.112	39.678	8.097	40.054	10.000	40.518
22.080	35.840	15.052	38.266	14.060	39.186	17.668	39.245	18.864	39.540
29.246	35.510	25.000	37.574	23.956	38.443	27.500	38.610	30.001	39.236
35.940	35.251	36.036	36.951	31.922	38.000	34.999	38.218	38.766	38.830
47.290	34.882	40.972	36.709	42.463	37.480	39.345	38.023	50.003	38.397
54.908	34.661	49.564	36.313	51.122	37.100	49.510	37.572	60.088	38.080
63.840	34.444	60.251	35.875	58.807	36.800	62.039	37.107	70.506	37.751
72.021	34.250	67.210	35.610	66.830	36.511	72.501	36.746	76.066	37.614
81.010	34.076	75.690	35.817	73.465	36.297	85.498	36.342	82.508	37.440

was repeated till the Λ_0 and the slope did not vary by more than 0.01%.

If it is assumed that $f^2 = 1$ for dilute solutions, the slope becomes $(L - A\Lambda_0)$. The contact distances are determined by solving the equation,

$$(L - A\Lambda_0) = E_1' \Lambda_0 H(b) - E_2' . G(b) - 6E'K(b) \quad \ldots (3)$$

where $b = e^2/aDkT$. The values of the functions H(b), G(b) and K(b) are available in literature[9]. Trial values of 'b' are used to calculate $(L - A\Lambda_0)$. From a plot of $(L - A\Lambda_0)$ vs b, the 'b' corresponding to the experimental value of $(L - A\Lambda_0)$ was interpolated. 'a' the ion size parameter was calculated from

$$a = e^2/bDkT = 560.47 \times 10^{-8}/bD \quad \ldots (4)$$

From the 'a' values K_A were calculated using the function[8]

$$K_A = 2.523 \times 10^{-8} \times \mathring{a}^8 e^b \quad \ldots (5)$$

The values of 'a' and K_A are given in Table 2.

TABLE 2—VALUES OF Λ_0, a AND K_A OF ALKALI METAL NITRATES IN DMSO AT 25°C

Salt	Λ_0	$\mathring{a}$	K_A	Sum. cryst. radii in Å
$LiNO_3$	38.3	4.112	3.260	1.81
$NaNO_3$	40.39	3.083	3.652	2.16
KNO_3	41.36	3.246	3.506	2.54
$RbNO_3$	41.74	3.331	3.449	2.69
$CsNO_3$	42.34	3.360	3.330	2.90

Solvated radii and solvation numbers of alkali metal and nitrate ions :

From the limiting single ion conductances of the alkali metal and nitrate ions obtained from the conductance data[10] the Stokes' radii (r_s) of the ions have been calculated. To obtain the corrected value, r_{Hx}, the method suggested by Nightingale[11] was employed. From a plot of r_s vs r_c (crystallographic radii) of the tetra alkyl ammonium ions[12] which are assumed to be unsolvated the actual radii r_{Hx} of the smaller ions in DMSO were interpolated from their r_s values. From the corrected radii (r_{Hx}) and the crystallographic radii (r_c) of the alkali metal and nitrate ions the solvation numbers were calculated[1]. The limiting single ion conductances, solvation numbers, r_c, r_s and r_{Hx} are given in Table 3. The plot of r_s vs r_c is shown in Fig. 1.

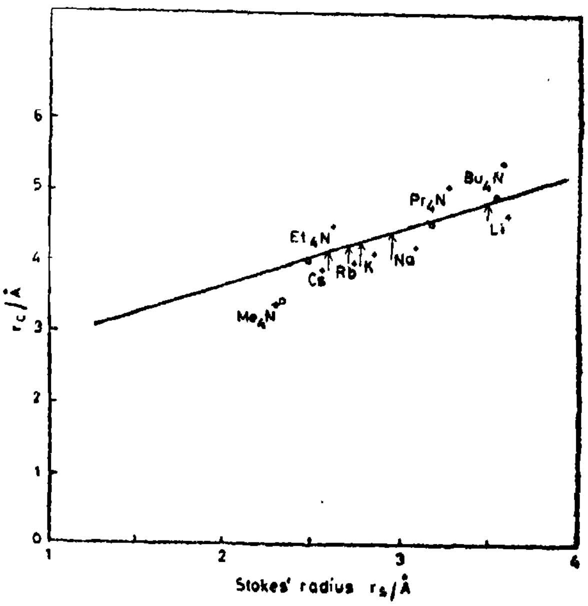


Fig. 1. Plot of Crystallographic radii (r_c) vs Stokes' radii (r_s)

TABLE 3—VALUES OF $\lambda_0^{\pm}$; r_s, r_c, r_{Hx} (in Å) AND SOLVATION NUMBERS OF ALKALIMETAL AND NITRATE IONS IN DMSO

Ion	$\lambda_0^{\pm}$	r_s	r_c	r_{Hx}	Solvation number
Li^+	11.80	3.186	0.60	4.78	4.30
Na^+	14.09	2.919	0.95	4.34	3.20
K^+	14.86	2.768	1.35	4.22	2.87
Rb^+	15.24	2.699	1.48	4.18	2.75
Cs^+	15.84	2.596	1.69	4.10	2.54
NO_3^-	26.50	1.552	1.20	3.33	1.89

It is clear that the extent of solvation is more for the cations than for the anion. This may be due to the stronger electrostatic interaction between the negative oxygen end of the S–O dipole of the DMSO molecule and the cation. It is reported that in dipolar aprotic solvents anions are only poorly solvated[13]. In DMSO the positive S centre is shielded by the two methyl groups and the steric hindrance thus reduces the solvation of anions through the S atom. Solvation decreases as r_c increases. It may be pointed out that the solvation number obtained for the Li^+ ion is greater than the value reported from NMR studies by Maxey and Popov[14]. The reason may be that the NMR method is sensitive only to the solvent molecules co-ordinated in the inner solvation sphere as reported by Streblow and Schneider[15]. Solvation numbers obtained in this work differ slightly from those reported by Ramgopal[1]. This may be due to the difference in the methods followed for the estimation of the single ion conductances. The extent of solvation is in the order

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ > NO_3^-.$$

Table 2 shows that the 'a' values are greater than the sum of the crystallographic radii for all the salts indicating the existence of solvation. The extent of solvation is greatest in the case of Li^+ ion, assuming that the NO_3^- ion is least solvated. The solvation numbers testify to this conclusion.

The K_A values which are a measure of ion-ion interaction are in the order $NaNO_3 > KNO_3 > RbNO_3 > CsNO_3 > LiNO_3$. The low K_A value of $LiNO_3$ may be ascribed to the lowered coulombic attraction of the solvated Li^+ ion caused by the large size of its solvo-dynamic unit (approximately equal to that of the Bu_4N^+ ion). Ion-pair formation is thus considerably reduced. From $NaNO_3$ to $CsNO_3$ eventhough the K_A values decrease, the differences are not much pronounced. This may be due to the almost near equal solvation members of these ions.

Acknowledgement

The authors are grateful to the Principal, Regional Engineering College, Calicut for providing the necessary laboratory facilities.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1219-1222

Carboxyalkylated Poly (Vinylalcohol) with Chloroacetic Acid and Polystyrenesulphonic Acid as Coagulant Aids in Nile Water Treatment

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Manuscript received 23 May 1978, revised 12 June 1980, accepted 7 August 1980

The effect of alum and ferric chloride on the turbidity, pH, alkalinity, residual aluminium or iron content and percent of algae removal in Nile Water treatment was investigated. They were also used in the least possible doses together with different amounts of polyelectrolytes such as carboxyalkylated poly vinyl alcohol (P. V. A.) with monochloroacetic asid (P. V. A. M. C. A.), dichloroacetic acid (P. V. A. D. C. A.) or trichloroacetic acid (P. V. A. T. C. A.) polystyrenesulphonic acid (P. S. S. A.) and also their mixtures. Their efficiencies were compared with those of P.V.A. and NaClo 600 SS -1.

THE relatively slow water flow in River Nile, and the absence of flood seasons after the building of Saad El-Ali in Aswan have resulted in little clay sedimental particles. The permitted sunlight to penetrate larger depth through water, has promoted the growth of algae and other organisms in varying amounts (enhanced by pollution from industrial wastes and sewage) and affected in some problems such as taste, odor, filter clogging, attachment to plant walls, toxic and hygienic effects.

The process of coagulation with the help of certain chemicals (which precipitate out insoluble, gelatinous flocculants, neutralize charged particles and combine with them) is reported to be more complete and rapid than will plain sedimentation[1]. Among the more commonly used coagulants are : aluminium sulphate, ferrous sulphate[2] together with calcium hydroxide and sodium aluminate[3]. Polyelectrolytes, such as polyacryamide[4,5] polyacrylic acid[6], sodium polyacrylate, sodium alginate, secondary or tertiary amines, and also quaternary ammonium or sulphonium salts and their mixtures[7], are claimed as coagulant aids which increase the efficiency of water purification plants.

While many inorganic salts, and natural organic substances such as gums, starches, algins and proteins can be used as flocculants, the synthetic organic water soluble polymers provide stricter control and usually an economic advantage.

The aim of this work was to investigate the validity of certain synthesized polyelectrolytes (mainly P.V.A.M.C.A., P.V.A.D.C.A., P.V.A.T.C.A. and PSSA)[8,9] as coagulant aids to remove fine turbidity and algae from Nile water, and comparing the results with those of P.V.A and Nalco 600 SS-1.

Experimental

Materials used :

Commercial alum. Aluminium sulphate with the specifications : Aluminium oxide content 16-18%, Ferric oxide content 0.9%, insoluble matter content not more than 1%, and arsenic content not more than 50 ppm.

Ferric chloride. Egyptian product with the specifications : Ferric chloride content 96% ; and foreign matter content not more than 1%.

Nalco 600 SS-1, imported from Italy, a viscous liquid, high molecular weight cationic polyelectrolyte. Laboratory tests showed that the *p*H of 5% solution is 4.05, phosphate about 0.3 mg/L, chlorides as Cl does not exceed 190 gm/l.

Poly (vinyl alcohol), product of Hoechst Company. Its specifications are mentioned elsewhere[8].

Carboxyalkylated poly (vinyl alcohol) with mono-, di- or trichloroacetic acids, of the following respective capacities : ml equiv/gm polymer 2.53, 2.86 and 2.628[8].

Polystyrenesulphonic acid, sulphur content 16.3%, capacity 4.4 ml equiv/gm, and *p*H of 1% solution = 2.7[9].

Methods :

Jar Test : Laboratory apparatus for determining optimum dosage of coagulating chemicals.

It is a multistirrer apparatus, consists of container 62×16×12 dimensions, equipped with electric stirrer having 4 vertical bars attached to each other, and switch, to control the number of revolutions per minute. Each bar has a horizontal plate to stir, the tested water in the beaker ($\frac{1}{2}$/–1 liter capacity) placed in the container. The height of the bars above the beakers is always kept at constant level.

In each run the coagulant was added to the beaker in 4 different doses upon stirring at revolutions of 120 r.p.m. After two minutes, the coagulant aid was added and after another two minutes, the speed slowed down to 40 r.p.m. for 20 min. Stirring was then stopped and the beakers were left 30 min for settling. Aliquots were then taken for study (5 cm below the surface in all measurements).

The used apparatus resembles approximately the field where flash mixer, clarifier and sedimentation zone act as rapid mixing, slow mixing and a period of time for settling respectively.

Turbidity in silica was determined by the help of photoelectric colorimeter "Lichtelectrisches kolorimeter, Model J. Nach Dr. B. Lange, NO. 11051, Berlin".

The total alkalinity as calcium carbonate mg/l was determined by the methyl orange indicator method[10].

A Beckman pH meter, H-2 Model G. pH-value, No. 5809, West Germany, and a glass electrode, were used for measuring the pH-value.

Residual aluminium was determined by the aluminon method[10].

Residual iron was determined by the thiocyanate method[11]. The algae count was carried out by the help of a special filtering funnel, Heamacytometer slide and a microscope. The filtering funnel conical in shape, made of pyrex or any other strong glass. It is divided into 2 parts, the first which has the conical shape is of 20 cm height and 12 cm in diameter. The second part is a tube of 10 cm long and 2.5 cm in diameter. It's end is fitted with a rubber stopper containing a capillary tube of 2 mm in diameter. The lower end of the funnel is filled with the filtering medium (fine sand with grain size range from 0.08-0.25 mm), 5 cm over the stopper which is covered by a disc of cloth to prevent sand from falling through the capillary tube. The Heamacytometer slide has been previously used for counting algae inspite of the fact that it is not a standard method[12]. Enumeration of the concentrated solutions of algae, collected from washing the sand by a known amount of water-free algae, was carried out by counting the number of viable cells in 6 fields using a Heamacytometer slide (Levy ultra plane, Cly Adams, 1/400 sq. mm, U.S.A.) and expressing the results as unit cells/ml.

Results and Discussion

Effect of Coagulants :

Experiments were carried out to determine the effective doses of alum and ferric chloride on Nile Water treatment.

The validity of poly vinyl alcohol, its carboxyalkylated product with chloroacetic acid and polystyrenesulphonic acid as coagulants, were investigated.

Quantities of alum, 5 ppm, or ferric chloride, 4 ppm probably were not effective for the floc to appear in appreciable quantities and sizes, so that the values of residual aluminium (0.35 ppm) and iron (0.4 ppm) in the filtered solution were the highest. Further increase in the added doses lead to an increase in floc formation (and consequently coagulation) and in the same time a decrease in the residual aluminium or iron in the filtered solutions. Doses higher than 55 ppm alum or 22 ppm ferric chloride (which seem to be somewhat expensive) cause an increase in the quantities of residual aluminium or iron, accompanied by coloration in case of ferric chloride.

However, in the two cases, the values of turbidity were 3,4 ppm in silica as compared with the initial values (50 and 52) in the raw Nile water. The alkalinity decreases (and the pH tends towards the acidic range) with increasing the dose of alum or ferric chloride. This is due to released H^+ ions to maintain electrical neutrality in the solution. Natural algae, predominantly carry negative charges, as indicated by their shift towards the positive electrode in the electrophoretic apparatus, may accumulate around the positive centers formed in the solution, and their per cent removal was 90% in both cases as shown in Fig. 1.

On the other hand, different doses of poly (vinyl alcohol), its carboxyalkylated product with chloroacetic acid or polystyrenesulphonic acid, as coagulants, produced no appreciable change in the properties of the studied Nile Water.

Effect of Coagulant Aids :

Optimum doses of alum (15 ppm) and ferric chloride (6 ppm) which produced appreciable decrease in turbidity and considerable algae removal (about 50%) in the treated Nile Water were chosen together with different types and doses of coagulant aids, such as Nalco 600 SS – 1, P.V.A., its carboxyalkylated, P.V.A.M.C.A., P.V.A.D.C.A., P.V.A.T.C.A. and PSSA and also their mixtures.

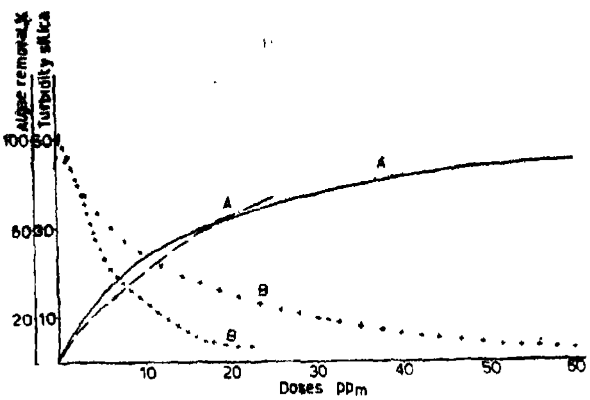


Fig. 1. Effect of aluminium sulphate as coagulant aid (A, B), and ferric chloride ($\bar{A}$, $\bar{B}$) on turbidity (B) and algae removal (A).

Results given in Fig. 2 show that Nalco 600 SS – 1 (1.6 ppm) together with the optimum doses of alum or ferric chloride, was a suitable coagulant aid resulting in about 87.2, 88% algae removal as compared with the maximum doses of only alum (50 ppm) or ferric chloride (22 ppm).

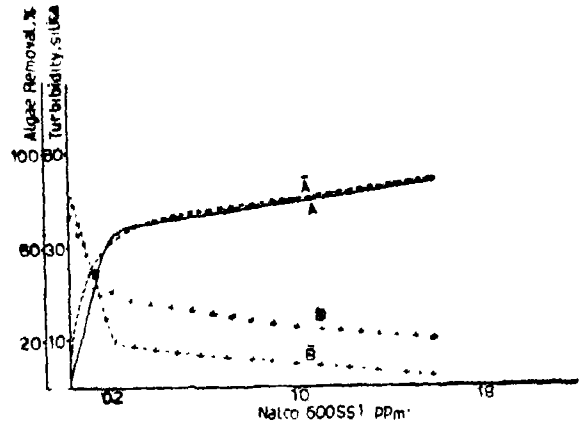


Fig. 2. Effect of Nalco 600SS1 as coagulant aid in presence of aluminium sulphate 15 ppm. (A, B) and ferric Chloride 6 ppm. ($\bar{A}$, $\bar{B}$) on turbidity and algae removal A, $\bar{A}$.

The decrease in residual Fe is greater tending to nearly zero ppm at 1.6 ppm Nalco, whereas the residual Al reaches 5 ppm at the same conditions. Moreover the alkalinity and *p*H decrease till 140, 7.6 in case of $FeCl_3$ and 142, 7.75 in case of $AL_2(SO_4)_3$ at Nalco doses of 0.2 ppm, after which they acquire relative decrease with higher doses of Nalco. The efficient quantities of P.V.A. as coagulant aid in Nile Water treatment were appreciably high (140-160 ppm).

At doses about 2 ppm of P.V.A.M.C.A., P.V.A. D.C.A. and also P.V.A.T.C.A., the respective percents of algae removal in presence of alum, and in the presence of ferric chloride were 75, 76.7, 85.6, 82.5, 80.0 and 78.3. They were also effective coagulant aids at doses of 4 ppm, creating floc particles of greater density with considerable settling rates. The addition of P.V.A.M.C.A., P.V.A.D.C.A. and P.V.A. T.C.A. lead to algae removal of 90, 98.2, 92.5 in presence of alum, and 92.5 for the three coagulant aids in case of $FeCl_3$. Curves in Fig. 3 represent the values obtained for P.V.A.M.C.A. The respective values of turbidity, *p*H and residual AL or Fe with the doses of the added P.V.A.M.C.A. (at a dose of 4 ppm) reached about 4, 7.3, 0.05 in case of alum and 5, 7.6, 0.02 in case of ferric chloride. Similar results were obtained in case of P.V.A.D.C.A. and P.V.A.T.C.A.

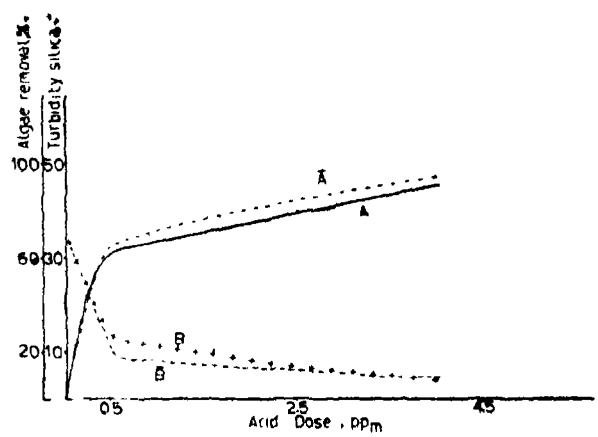


Fig. 3. Effect of carboxyalkylated poly vinylalcohol with monochloroacetic acid and aluminium sulphate 15 ppm. (A, B) and ferric chloride 6 ppm. ($\bar{A}$, $\bar{B}$) on turbidity (B, $\bar{B}$) and algae removal (A, $\bar{A}$).

On the other hand, the increasing per cent of algae removal with the doses of PSSA, reached 90% at 4-5 ppm in case of alum and 92.5% at 3.5-5 ppm in the presence of ferric chloride.

The respective values at 2 ppm were 81.2 and 83.3%. Higher doses lead to an increase in the per cent of algae removal, whereas the residual aluminium or iron was always less than 0.05 ppm accompanied with fragile and tough flocs smaller doses constructed compact and settable flocs. Doses of 4 ppm from mixtures of PSSA and P.V.A.M.C.A., P.V.A.D.C.A. or P.V.A.T.C.A. in equal weights produced percents of algae removal about 94, 93.4 and 94.3 respectively (in presence of alum). At mixture doses of 2 ppm, the respective values of algae removal 85, 86.9 and 86.3% are comparable with those in case of Nalco 600 SS – 1.

Because Nile Water varies and fluctuates widely in quality, needed coagulation and flocculation are best determined in practice by trial.

Required coagulant dosage is usually found by Jar tests performed in all laboratory stirring device. Since coagulation depends on so many variables that are themselves interdependent, as many testing parameters as possible are necessary to investigate, by changing one parameter, while the others being kept constant. The experiments were carried out through 2 years from 8/1971 till 8/1973 over a wide range of temperatures from 14-27° and algae count from 6800-15000 units/ml. The beginning of each curve (zero point) represents the state and quality of the raw Nile Water. The experiments were repeated several times and there is no appreciable change in the results.

It is probable that such cationic polyelectrolytes of opposite charge to the algae cause floculation by reducing the electrokinetic potential of solid surfaces carrying negative charges and lead therefore to coagulation.

Coagulation was therefore improved by such synthesized coagulant aids, that is, substances that increase the critical mass of colloids and speed up coagulation. The validity of such coagulant aids for water with little turbidity like Nile Water after the building of High Dam and the absence of flood seasons is very important since little turbidity may not coagulate as easily as well as water of moderate turbidity.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1223-1225

The Electrodeposition of Zinc and Nickel in the Presence of Acetylacetone : The Behaviour of the Ligand as Both an Inhibitor and a Depolarizer

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Manuscript received 2 November 1979, revised 10 April 1980, accepted 9 September 1980

The electrodeposition of zinc and nickel from aqueous solutions is investigated in the presence of acetylacetone at pH values of 4.0 and 5.2 respectively. The current efficiency of the zinc and nickel deposition is dependent on the concentration of acetylacetone and the applied current density. The ligand behaves as a surface active substance as well as a depolarizer. The surface activity is more pronounced in the case of the nickel deposition whereas the ligand is reduced during the zinc deposition. The cathodic behaviour of metal ions is compatible with the suggestion that the ligand could manifest itself as both an inhibitor and a depolarizer. The throwing power of the metal deposition baths is markedly influenced by the addition of acetylacetone.

THE theory of complex formation was the first quantitative treatment that led to an understanding of the role of surface active substances (S.A.S.) in electrode processes[1]. The adsorption of the S.A.S. on the electrode followed by its coordination with the metal ion was the reason behind the inhibition effects of the electrode process. It has been reported[2] that an increase in the S.A.S. concentration would be accompanied by a parallel increase in polarization up to a certain concentration above which polarization will attain a constant value.

Several types of organic compounds were used as S.A.S. which included quaternary ammonium salts, sodium salts of sulphonic acid derivatives, and long chain alcohols[3]. Various theories were suggested to explain the effect of the S.A.S. on the electrode processes[4].

Interest in the versatile chemistry[5] of acetylacetone prompted a study of its action as S.A.S. since it could behave as a depolarizer[6], as well as a strong chelating ligand[5].

Experimental

Materials : All chemicals used were of reagent grade. In the electrodeposition of nickel the bath consisted[7] of $NiSO_4.7H_2O$ (75 g/1), NaCl (15g/1) and H_3BO_3 (15 g/1), while that for zinc contained[7] $ZnSO_4.7H_2O$ (215 g/1), $Al_2(SO_4)_3.18H_2O$ (30 g/1) and $Na_2SO_4.10H_2O$ (50 g/1).

Efficiency measurements : The cathode current efficiency was estimated by measuring the total quantity of electricity passed using a copper coulometer.

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The efficiency of the hydrogen evolution during the electrodeposition was separately determined using a hydrogen gas coulometer. This was carried out at the same experimental conditions at which the efficiency of the metal deposition was measured.

Polarization measurements : These measurements were carried out galvanostatically. The electrode potential was measured against a saturated calomel electrode.

Throwing power : The throwing power (A) of the studied baths was calculated[8] from the weight ratio of the deposit on two cathodes of equal surface area (2 cm × 1 cm) but placed at different distances from the anode (15 and 40 cm). Thus,

$$A = \frac{W_1}{W_2} . 100$$

where W_1 and W_2 refer to the weight of the deposit at the far and near cathode respectively (Fig. 1).

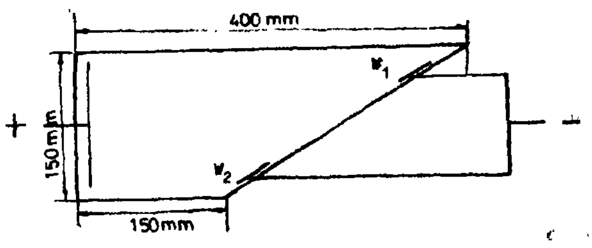


Fig. 1. Throwing power cell.

The plating time of the unstirred bath was 45-60 minutes. A freshly prepared bath was used for each experiment. The nickel and zinc baths were maintained at pH 5.2 and 4.0 respectively.

TABLE 1—THE CURRENT EFFICIENCY OF METAL DEPOSITION AND HYDROGEN EVOLUTION AT DIFFERENT CURRENT DENSITIES AND ACETYLACETONE CONCENTRATIONS AT 30°C

Ref. No.	Metal ion	Current density (mA cm^{-2})	Acetylacetone Concentration (mole/l) —		0.001		0.005		0.010		0.050		0.075		0.10	
			M%	H_2%	M%	H_2%	M%	H_2%	M%	H_2%	M%	H_2%	M%	H_2%	M%	H_2%
1.	Zinc	5.0	94.4	5.0	96.0	2.5	97.0	2.0	96.0	2.0	92.1	1.5	90.5	2.0	87.0	4.0
2.		10.0	94.4	5.0	97.5	1.5	99.0	—	100.0	—	80.2	3.0	76.0	4.0	74.6	8.0
3.		15.0	94.6	5.0	97.8	1.5	100.0	—	100.0	—	91.1	3.0	80.5	5.0	78.5	9.0
4.		20.0	94.5	4.0	98.0	1.0	100.0	—	100.0	—	97.0	1.5	92.0	3.5	89.6	5.0
1.	Nickel	5.0	88.2	11.0	(a)	10.0	(a)	9.0	(a)	8.0	91.7	6.0	88.2	4.0	81.7	3.5
2.		10.0	81.6	18.0	(a)	12.0	(a)	9.0	(a)	6.0	97.9	2.0	97.4	1.5	96.7	2.5
3.		15.0	50.0	48.5	(a)	30.0	(a)	21.0	(a)	10.0	95.8	2.5	95.6	2.5	95.8	3.5
		20.0	24.6	74.0	(a)	52.0	(a)	30.0	(a)	13.0	96.4	2.5	98.8	1.0	97.2	2.0

(a) Spongy and poor quality deposit which is difficult to handle was obtained.

Results and Discussion

The dependence of the cathodic current efficiency, relating to metal deposition, on both the acetylacetone concentration and the current density is shown in Table 1. The overall cathodic action during the deposition of zinc or nickel in the presence of acetylacetone could comprise the following competing processes, (*i*) metal ion discharge, (*ii*) hydrogen evolution, and (*iii*) acetylacetone reduction. The relative contribution of each of the three processes to the overall cathodic reaction is evident from the data of Table 1. For zinc deposition, there is a slight increase in current efficiency with increase of acetylacetone concentration up to a certain level, beyond which a gradual decrease occurs. In the case of nickel solution, a considerable increase in efficiency is observed especially at high current densities. This observation is explained by the mixed effects (i-iii). Thus, acetylacetone could be readily reduced on the deposited zinc electrode which is not the case for nickel[6].

The zinc deposition is expected to take place from the hydrated metal ion and not from its acetylacetonate complex which could not be formed at this acidic condition[5]. However, nickel deposition can occur, under the experimental condition, from both the hydrated ion and the trimeric nickel acetylacetonate[5] ($[Ni(acac)_2]_3$; Hacac = acetylacetone). The latter is known to be formed at nearly neutral or slightly acidic conditions[5].

In the case of zinc deposition in the presence of low concentration of acetylacetone the main role of the ligand is the inhibition of the hydrogen evolution. This conclusion is supported by the decrease in current efficiency of hydrogen evolution at low concentrations of acetylacetone and by increase in hydrogen evolution at higher concentrations (Table 1).

The situation with nickel is different from that of zinc. The former is expected to have a low hydrogen overpotential[9] and consequently the carbonyl and carboxy compounds are difficult to be reduced on it. Accordingly, the inhibitor role of acetylacetone is manifested at higher concentration. At low values of current densities, however, a slight contribution of acetylacetone as a depolarizer could account for the observed decrease in the efficiency of nickel deposition at acetylacetone concentrations higher than 0.05*M*.

The foregoing arguments could be substantiated by the polarization curves shown in Fig. 2. In the case of zinc, the presence of acetylacetone produced an obvious depolarization effect especially at low current densities where the cathodic potentials are less negative than those of the hydrogen evolution. The inhibition effect of acetylacetone became dominant at more negative potentials and higher



Fig. 2. Cathodic polarization curves for the deposition of nickel and zinc from solutions containing acetylacetone.

current densities as the main cathodic process is only metal deposition. This behaviour is in accordance with the results of the current efficiency

measurements of Table 1. The corresponding measurements for nickel indicate that the effect of acetylacetone on the cathodic polarization of nickel deposition appears to be mainly an inhibition one. The shift of the cathodic potentials towards higher values by the addition of acetylacetone does not necessarily imply that the hydrogen evolution process becomes easier. This is in agreement with the observed increase in the deposition efficiency of nickel in the presence of acetylacetone (Table 1).

It is worth mentioning in this connection that the cathodic deposition of zinc takes place in the region of its zero charge point whereas that of the nickel is shifted to the negative side[10]. This observation is explained by the adsorption of the nickel acetylacetonate (via the residual positive charge on the metal ion) which will consequently favour the nickel deposition process rather than the hydrogen evolution on the nickel cathode. In the presence of zinc ions, however the free acetylacetone molecule could be adsorbed, which leads to its reduction ; a process that leads to the observed decrease in the efficiency of the metal deposition.

The final distribution of a certain metal deposit is a function of factors like the polarizability and the variations in the current efficiency[11]. The effect of the latter factor on the zinc deposition indicates that the throwing power increases at low concentration of acetylacetone, while at a higher concentration of the ligand the phenomenon is reversed (Table 2). The polarizability is almost unchanged by the addition of acetylacetone which leaves the current efficiency as the only operating factor. The throwing power of the studied nickel bath is decreased by the addition of acetylacetone. The data of Table 1 indicate that the variation of the current efficiency with the current density should result into lower values for the throwing power (Table 2). In this case the polarizability increases by the addition of acetylacetone (Fig. 2).

TABLE 2—THE EFFECT OF ACETYLACETONE ON THE THROWING POWER OF ZINC AND NICKEL BATHS AT 20 mA cm^{-2} AND 30°C

Ref. No.	Acetylacetone concentration (mole/l)	Throwing power % Zinc	Throwing power % Nickel
1.	—	9.0	31.2
2.	0.001	14.0	(a)
3.	0.005	15.0	(a)
4.	0.010	13.5	(a)
5.	0.050	10.4	27.0
6.	0.075	10.5	17.7
7.	0.100	10.8	13.2

(a) See footnote of Table 1 for significance.

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J. Indian Chem. Soc.,
Vol. LVII, December 1980, pp. 1226-1231

Kaolinite Oxamyl Interactions

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Manuscript received 16 May 1979, accepted 25 August 1980

The adsorptive behaviour of oxamyl with H-, Na- and Ca- kaolinites was studied. The effect of time on adsorption showed that process was diffusion controlled. Kinetic studies showed that reaction was of first order. Maximum adsorption occurred at pH 6.5. The adsorption isotherms and desorption experiments provided evidence for a *partly chemisorption and partly physical adsorption of oxamyl on clay surface.* Inferences on the protonation of the carbonyl oxygen of the oxamyl molecule by H^+ ions on kaolinite and/or the coordination of the metallic cations of kaolinite to the carbonyl of amide group found support from adsorption isotherms, thermodynamic parameters, X-ray and IR studies.

NUMEROUS organic chemicals with a wide range of biochemical, chemical and physical properties are being introduced as pesticides and plant growth regulators in modern agriculture. Since these chemicals play a vital role in biochemical and pesticidal processes in plants and soils, it is important that the fate of such chemicals must be thoroughly investigated so that they can be used with utmost advantage and least adverse effects. In this regard interest attaches to the adsorption and complexation of pesticides with clays.

Recently the fate and behaviour of pesticides in soils is a subject of great deal of research[1]. Effective pesticidal action of organic chemicals in soil is governed by a number of factors one of which is adsorption on soil colloids. The nature of adsorption affects the ease of pesticidal chemical movement and plant availability, their persistence, degradation and toxicity. So, any investigation on the interaction of pesticidal chemicals with soil or soil constituents besides throwing some light on the fundamental behaviour of organic chemical also will be of great practical importance. While the interaction and adsorption of ionic pesticides on clay surface has been extensively studied[2], the relatively less work was done on the reaction mechanism of non-ionic pesticides on soil colloids.

Clay minerals constitute the most reactive portion of soil. Clay provides heterogeneous chemical spots in the form of sorbed water around cations[3], lattice surface oxygen[4], electron accepting sites[5] and transition metals in higher valency states. Thus an organic chemical may be adsorbed on the clay surface by ion exchange, protonation, hydrogen bonding, coordination[6], ion-dipole interaction, van der Waal's forces, charge transfer complex and hemisalt formation[7].

Oxamyl {methyl 2-(dimethylamino)-N-[{(methylamino) carbonyl}oxy]-2-oxoethanimidothioate}, a formulation of DuPont de Nemours & Co. Inc., Wilmington, U. S. A. is a recently introduced broad spectrum non-ionic pesticide used as nematocide[8,9].

Adsorption isotherms, X-ray, infrared and thermodynamic studies can be used to provide information on the mechanism of interaction of organic pesticides with clays. The main objective of the present investigation was to investigate the mechanism of adsorption and interaction of oxamyl with acid and base saturated kaolinites in dilute clay-water suspensions. It was considered that such a study will be useful in the efficient utilization of chemical (oxamyl) in kaolinitic soils.

Experimental

Kaolinite used in these studies was from Bath, South Carolina, and was a monomineralic standard of Project No. 49 of the American Petroleum Institute. Less than 2 μm clay fraction was purified by sedimentation and centrifugation. The suspension was then converted into chloride free sodium and hydrogen ion saturated kaolinites by Aldrich and Buchanan's method as described elsewhere[10]. Calcium saturated kaolinite was prepared from the sodium form, by treating it with $CaCl_2$. The clays were used for experiments immediately after their preparation. The concentration of all the suspensions varied from 14.0 to 15.7 gl^{-1}. The cation exchange capacity (CEC) as determined by Ganguli's method was 106 μ equiv/g clay.

To study the effect of time experiments were conducted taking 10 ml of appropriate clay-water suspensions in their H-, Na- and Ca-forms in several glass stoppered tubes and were treated with 5 and 15 ml of oxamyl solution (1000 μg/ml), the volume was made to 25 ml with distilled water. The samples were kept in contact for 3, 6, 9, 15, 18, 24, 27, 30, 33, 48, 54 and 72 hr with continuous shaking in a

mechanical shaker. The mixtures were then centrifuged and the oxamyl in the supernatants was estimated spectrophotometrically at 435 nm[18]. The amount of oxamyl adsorbed at various intervals of time was obtained than the amount of oxamyl added minus remaining in the supernatants.

To study the *p*H effect adsorption experiments were conducted at *p*H values adjusted to 2, 4, 6, 6.5, 7, 8, 10 and 12 by 0.01*M* HCl or 0.01*M* NaOH as required. For *p*H study, 10 ml of H-, Na- and Ca- saturated kaolinite suspensions and 5 and 15 ml of oxamyl solutions (1000 μg/ml) were taken in glass stoppered tubes and the tubes were shaken for 33 hr in a mechanical shaker. The samples were then centrifuged and oxamyl adsorbed and remaining in the supernatant was estimated and calculated as above.

Adsorption experiments were conducted by taking 10 ml of the appropriate kaolinite suspensions in H-, Na- and Ca- forms, in a large number of glass stoppered tubes, adding various amounts (0 to 15 ml) of standard oxamyl solution (1000 μg/ml), making up the volume to 25 ml with distilled water and shaking for 30 hr at 20 and 50°. Oxamyl in the centrifuged supernatants was estimated as described above. Adsorption isotherms were plotted between the equilibrium concentration (mM) of oxamyl in the suspensions and amount of oxamyl adsorbed (μ mole/g clay) (Fig. 3).

In the desorption experiments 10 ml of oxamyl complexed kaolinites were treated with water, 1 ml of 0.1*M* KCl and 0.1*M* $BaCl_2$ respectively, the volume adjusted to 25 ml with water and the samples were shaken for 33 hr, then oxamyl estimated as above. The results are shown in Table 2.

The results of adsorption were correlated with X-ray and IR studies. For X-ray analysis less than 2 μm acid and base saturated suspensions of kaolinite and their complexes with oxamyl were allowed to dry on microglass slides to form well oriented flat layers. X-ray diffractions were recorded on a General Electric Diffraction unit at a speed of 0.4 degree 2θ per minute using filtered CuK_α radiation. For IR analysis thin self supporting films of the sample were prepared by drying the kaolinite water suspension (H-, Na- and Ca- forms) and their complexed clay-water suspension at room temperature on polythene sheets. The spectra of the samples and oxamyl (pure) were recorded in the range 4000 to 400 cm^{-1}. on a Beckman IR-20 double beam spectrophotometer.

All experiments were done in duplicate with suitable reagent and clay blanks.

Results and Discussion

Adsorption of oxamyl as a function of time on H-, Na- and Ca- saturated kaolinites for two concentrations of oxamyl is shown in Fig. 1. The adsorption of oxamyl was found to be increased with time upto an interval of 33 hr after which it became constant. Such a slow rate of attaining the equilibrium indicates that process is at least partly of chemical nature[18]. On applying the simple kinetic rate laws, the calculation of the rate constants at different time intervals and concentrations gave values as given in Table 1, which indicated that the adsorption reaction was of first order and the half time of adsorption ($t_{1/2}$ values) increased

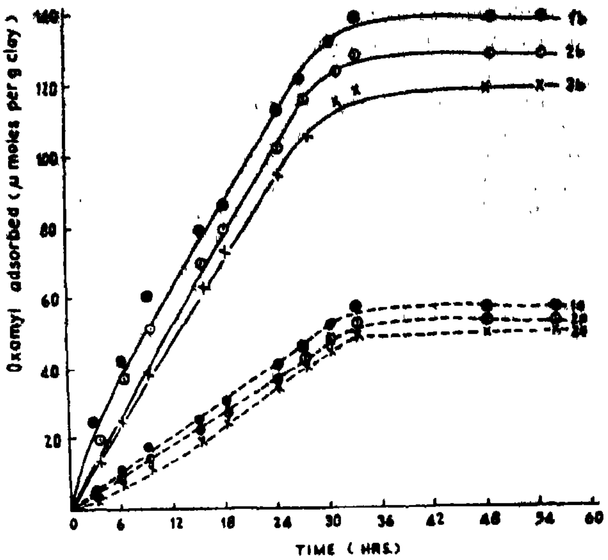


Fig. 1. Effect of time on the adsorption of oxamyl by kaolinites (o) hydrogen form (●) sodium form, (x) calcium form. Oxamyl added per g of clay. 1(a) 146μ mole 1(b) 438μ mole, 2(a) 169μ mole, 2(b) 480μ mole, 3(a) 150μ mole and 3(b) 449μ mole.

Table 1—Effect of Time on the Adsorption of Oxamyl with H-, Na- and Ca- saturated Kaolinites at 20°C

Form of Clay	μ moles of oxamyl added per g clay	Rate constant $k \times 10^6$ (sec^{-1})	Half life period ($t_{1/2}$) of adsorption in hr
H-kaolinite	168	2.27	84.9
	480	2.20	87.5
Na-kaolinite	146	2.35	81.9
	438	2.30	83.7
Ca-kaolinite	152	2.20	87.5
	456	2.08	92.4

Table 2—Desorption of Oxamyl by Different Electrolytes from the H-, Na- and Ca- saturated Kaolinite—Oxamyl Complexes

Form of Clay	Oxamyl adsorbed μ mole/g clay	Oxamyl desorbed (μmole/g clay) by H_2O	KCl	$BaCl_2$
H-kaolinite	184	38	62	62
Na-kaolinite	188	47	86	68
Ca-kaolinite	125	37	81	84

with increasing oxamyl concentration, suggesting a diffusion controlled process[14].

The effect of pH on the adsorption of oxamyl on kaolinites is given in Fig. 2. Both at higher and lower concentration of oxamyl added, adsorption increased with pH up to a value of pH 6.5 and beyond this value the adsorption has a tendency to decrease. The pK value of oxamyl in distilled water as determined by the conductivity method was 6.2. Its potentiometric titration with 0.001*M* HCl and 0.001*M* NaOH showed that oxamyl behaves as an ampholite with pK_1 value 4 and pK_2 8 (Fig. 4). As expected, the maximum adsorption

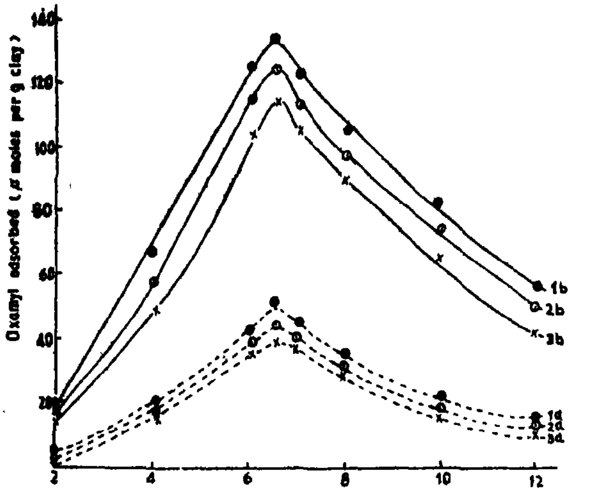


Fig. 2. Effect of pH on the adsorption of oxamyl by kaolinites, (o) hydrogen form, (●) sodium form, (x) calcium form. Oxamyl added per g of clay. 1(a) 146μ mole, 1(b) 488μ mole, 2(a) 160μ mole, 2(b) 480μ mole, 3(a) 150μ mole and 3(b) 449μ mole.

occurs in the vicinity of pK value (6.2). It appears that at pH values lower than 6.5 oxamyl and at pH values greater than 6.5. Na^+ oxamyl are formed by interaction with H^+ (from HCl) and Na^+ (from NaOH) ions. These ion complexes are not adsorbable on acid and base saturated kaolinites. This is supported by desorption studies. In the absence of competition from H^+ or Na^+ ions at pH 6.5 a direct association of the pesticide with the cations on the clay surface probably occurs giving maximum adsorption[15,16].

The empirical Freundlich relationship is used to describe the oxamyl adsorption results on kaolinite. The linear form of the equation is :

$$X/m = KC^{1/n} \text{ or } \ln X/m = \ln K + 1/n \ \ln C$$

where X/m = oxamyl adsorbed (μg/g clay), C = equilibrium concentration in solution (μg/ml), K and 1/n are constants which characterize the adsorption capacity for the oxamyl. A plot of ln X/m against lnC gave linear curves in all the cases at both the temperatures (Fig. 5). K is the amount adsorbed for a unit equilibrium concentration of oxamyl and 1/n the slope is a measure of the intensity of adsorption reflecting the degrees to which adsorption is a function of concentration. The values are given in Table 3.

TABLE 3—FREUNDLICH CONSTANTS FOR ADSORPTION OF OXAMYL ON H-, Na- and Ca-KAOLINITES AT 20 AND 50°

Nature of Clay	Temp. (K)	Freundlich Constants	
		K	1/n
H-kao.		1089±2.0	0.545±0.005
	323	1072±1.8	0.500±0.002
Na-kao.	293	1144±2.6	0.565±0.004
	323	1134±1.9	0.580±0.005
Ca-kao.	293	1036±3.1	0.525±0.002
	323	1002±0.8	0.490±0.008

± Standard error of estimate.

An examination of Table 3 indicated that the values of the sorption intensity, 1/*n* were always of less unity. These were indicative of a significant non-linearity in the isotherms (L type isotherm) and an exponential decrease in the sorption energy as the proportion of adsorption sites saturated with oxamyl became larger[17]. The non-linearity varied with the type of cation of kaolinite and the temperature. These factors also influenced the adsorption of oxamyl. This found further confirmation from the values of K, Freundlich constant. The higher values of K at 20° than at 50° in all cases pointed to a decrease in the adsorption of the pesticide with rise in temperature i. e., the interaction of oxamyl with H-, Na- and Ca-kaolinites was of an exothermic nature and followed the order Na-kao > H-kao > Ca-kao.

Adsorption of oxamyl on H-, Na- and Ca-saturated kaolinite suspensions (1.40-1.57% w/v) in the equilibrium concentration range 0 to 2.2 mM at 20 and 50° yielded isotherms as shown in Fig. 3. An examination of adsorption isotherms revealed that they were similar to class 'L' as defined by Giles *et al*[18]. This kind of isotherm may arise due to minimum competition of solvent for sites on the adsorbing surface. The slope of isotherm steadily decreases with rise in solute concentration because vacant sites become less accessible with the progressive covering of the surface. The curvilinear isotherm suggests that the number of available sites for the adsorption become a limiting factor[19]. Fig. 3 also showed that a greater amount of oxamyl is adsorbed by the base saturated kaolinites than the acid saturated and followed the order Na-kao > H-kao > Ca-kao. Further an increase in temperature from 20 to 50° decreased the adsorption, which may be due to increased desorption by increasing the thermal energy of adsorbate. The uniformity of

the curves at both the temperatures also showed that the temperature does not change the nature of the reaction but influence the number of adsorption sites and/or affinity for oxamyl.

The results of desorption (Table 2) indicate that the part of the oxamyl adsorbed on H-, Na- and Ca-kaolinites can be desorbed by water or solutions of inorganic salts, indicating that the appreciable adsorption of oxamyl on clay surface occurs by ionic interactions and by long range attractive forces.

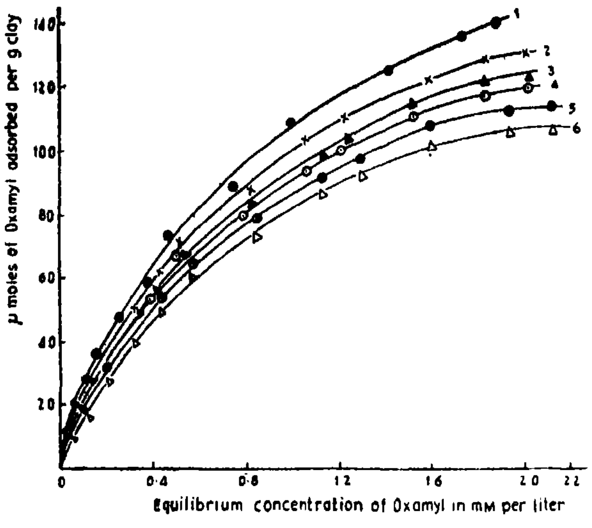


Fig. 3. Adsorption isotherm of oxamyl on H(x), Na(●), Ca(▲) at 30° and on H(◐), Na(⊙) and Ca(△)—kaolinites at 50°.

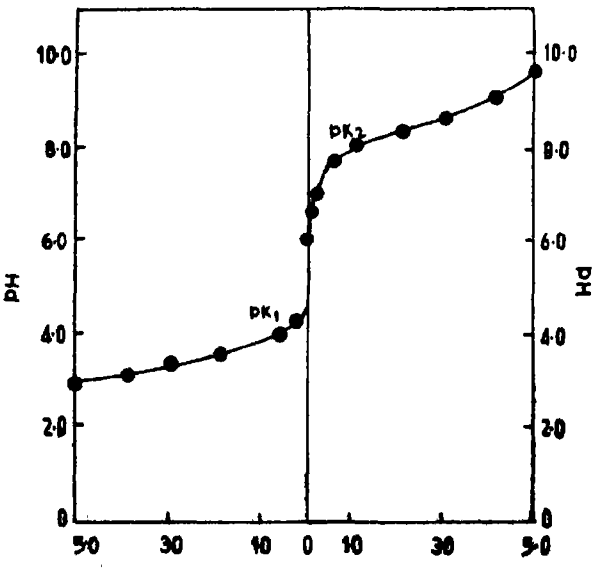


Fig. 4. Variation of pH during treatment of oxamyl with acid or alkali.

Above propositions were also supported by thermodynamic parameters. From the adsorption curves (Fig. 3) the thermodynamic equilibrium constant (Ko), the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes were calculated according the Biggar and Cheung method[20]. The values are recorded in Table 4.

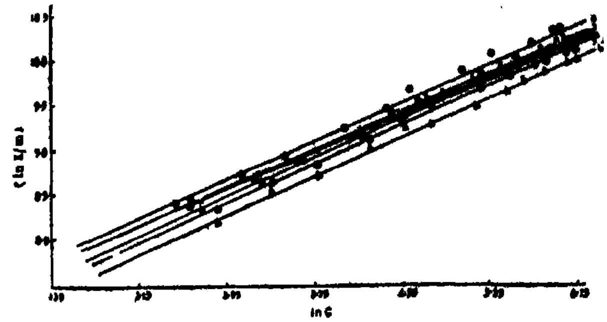


Fig. 5. Freundlich isotherms of oxamyl adsorption on H(x), Na(●), Ca(▲) at 30° and on H(◐), Na(⊙) and Ca(△) kaolinites at 50°.

TABLE 4—THERMODYNAMIC PARAMETERS FOR THE OXAMYL ADSORPTION ON H-, Na- and Ca-KAOLINITES AT 20 AND 50°

Thermodynamic parameters	H-kaolinite		Na-kaolinite		Ca-kaolinite	
°C	20	50	20	50	20	50
Ko	2026	863	2284	932	1808	802
ΔG°(K J/mole)	−18.55	−18.16	−18.79	−18.36	−18.27	−17.96
ΔH°(K J/mole)	−22.39		−22.94		−21.25	
ΔS°(J/mole)	−18.10		−14.17		−10.17	

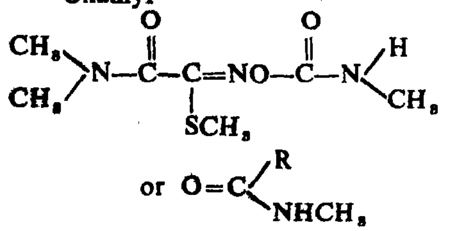
An examination of Table 4 showed that the values of Ko were always higher than unity, i. e., oxamyl had a preference for kaolinite surface. The values confirmed the deductions that adsorption of oxamyl on kaolinites decreased with a rise in temperature and order of adsorption was Na-kao>H-kao>Ca-kao.

The values of ΔG° were negative at both the temperatures and increased with rise in temperature pointing towards the spontaneity of the reaction with a greater affinity of kaolinites for oxamyl. The values of ΔG° showed that for the oxamyl driving forces of reaction, the strength of adsorption and degree of order attained during adsorption reaction is Na->H->Ca- kaolinites.

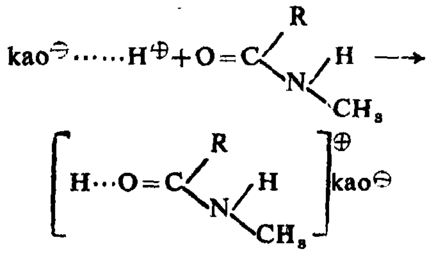
The enthalpy changes (negative value ΔH°) showed that the reaction is of exothermic nature with a binding of the oxamyl molecules to the acid and base saturated kaolinites and adsorption occurs through bonding mechanism[21]. The values of ΔH° also confirmed our earlier inferences on the affinity of oxamyl. The negative value of ΔS° indicated that there is no configurational changes and the complexes of oxamyl with kaolinites are stable[22].

Association, fixation, or immobilization of the pesticide molecule as a result of adsorption resulted in the loss of the degrees of the freedom of the pesticide molecule thereby producing negative entropy effects.

Oxamyl

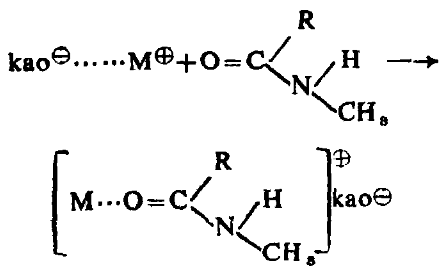


is a non-ionic neutral molecule, possesses a slight polarity at the nitrogen and oxygens of amide group due to electrometric and resonance effects. These nitrogen and oxygens of amide group may thus interact with suitable spots on the kaolinites. *It appears that on H-kaolinite oxamyl is adsorbed* by protonation at the edges and basal planes as :

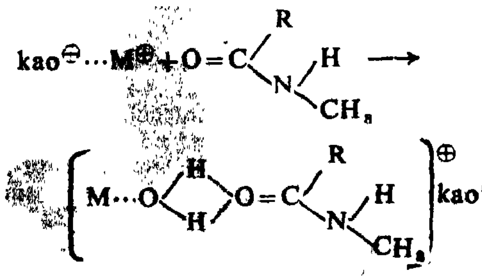


... (1)

The base saturated kaolinites carry exchangeable cations which provide excellent sites for linking of polar organic molecules through a direct coordinated reaction[7,22] to the oxygen of the carbonyl group as[23] :



... (2)

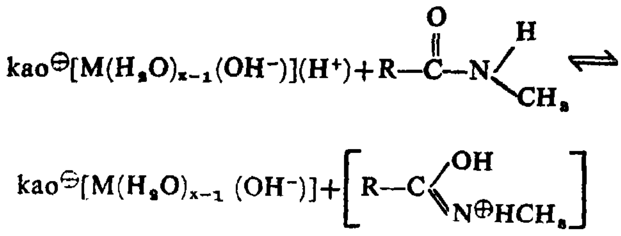


... (2a)

Further the dissociation of water molecules in contact with exchangeable cations bring about proton formation[24,25], the degree of hydrolysis depending upon the polarising power of the cations.

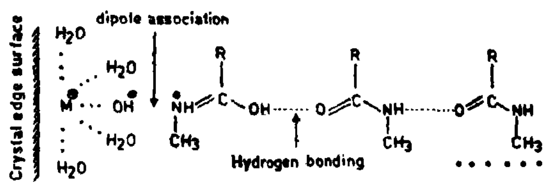
$$[M(H_2O)_x]^{n+} \rightleftharpoons [M(OH^-)(H_2O)_{x-1}]^{(n-1)} + H^+ \quad \ldots (3)$$

The protons released[26] binds the oxamyl to the clay surface by ionic bonding as :

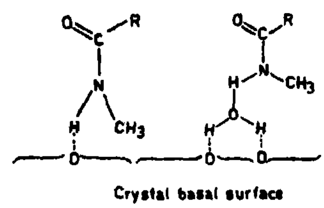


... (4)

The desorption data indicate that besides chemisorption some physical adsorption also occurs. The physical adsorption may occur through formation of hydrogen bonds between the protonated molecules on the mineral surface and the neutral oxamyl molecules at crystal edge and basal surface as postulated by Stutzmann and Siffert[27] for the adsorption of acetamide molecules on the *montmorillonite* surface as :



.... (5)



...... (6)

These mechanisms were supported by IR and X-ray studies. A shift of bands at 1670 cm^{-1} ($\Delta\nu = -15$ to -20 cm^{-1}) attributed to a >C=O stretching vibration, at 1680 cm^{-1} ($\Delta\nu = +10$ to $+15$ cm^{-1}) attributing to C=N stretching during complexation of oxamyl with H-, Na- and Ca- kaolinites were recorded. These spectral shifts confirm the mechanisms 1 to 4 as discussed by Bellamy[28]. Basal expansion of 0.20, 0.18, 0.22 nm (X-ray studies) during interaction of oxamyl with H-, Na. and Ca- saturated kaolinites respectively, confirms the adsorption of oxamyl with a flat orientation.

Acknowledgement

Thanks are due to Prof. S. S. Gupta, Principal, D. S. College, Aligarh for providing laboratory facility and encouragement and to Sri A. K. Chaturvedi for kind cooperation.

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NOTES

Metal Chelates with *bis*-2(imino)-4-Thiazolidinone

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Manuscript received 8 December 1979, revised 27 May 1980, accepted 9 September 1980

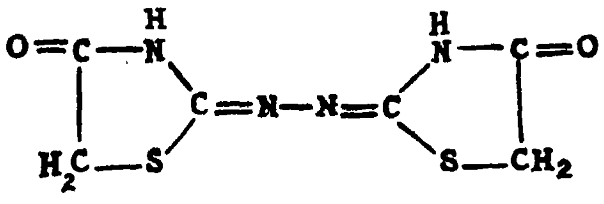
THE preparation of metal chelates with N, N'-di(thiocarbamoyl) hydrazine has been reported by us earlier[1]. *Bis*-2(imino)-4-thiazolidinone (H_2-BITZ) which is a derivative of N, N'-di(thiocarbamoyl) hydrazine has been synthesized by adopting the literature method[2]. In order to get structurally important chelates and also to study their antifungal activity attempts were made to synthesize metal chelates with H_2BITZ.

Experimental

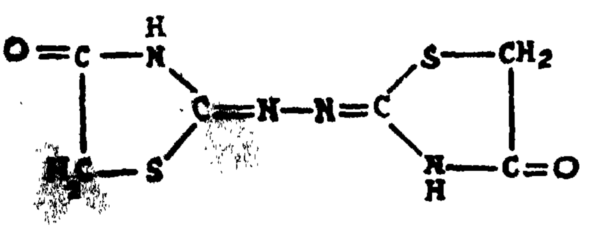
Bis-2(imino)-4-thiazolidinone (H_2BITZ) was prepared by a known method[2], m.p. 260° (literature value 260°). Metal chelates prepared in the present investigation are similar to those as reported earlier[3]. Elemental analyses of these chelates were done according to standard procedures[4]. The magnetic, electronic and i. r. spectral measurements of the chelates were carried out as described previously[3].

Results and Discussion

The ligand can be structurally represented in two different ways as shown in Figs. I and II.



I



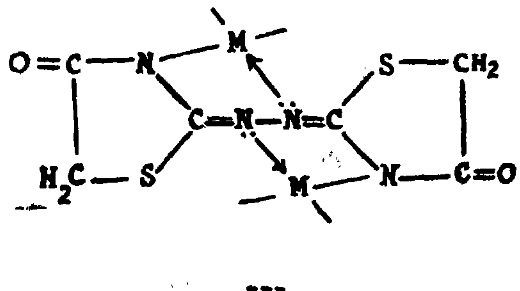
II

All the complexes isolated with divalent metal ions occur as inner complex salts with metal to ligand ratio 1 : 1. In other words, the ligand loses two protons during complex formation. This behaviour along with i.r. spectral data lead us to believe that the ligand predominantly occurs in the structural form II rather than I.

The series of strong bands which are observed in the spectra of N,N'-di(thiocarbamoyl) hydrazine[1] in the region 3300 cm^{-1} and attributed to NH_2 stretching vibrations strikingly disappear in the newly synthesized ligand. The significant features of the spectra of the ligand in this range are the appearance of two to three bands at a relatively lower frequency region 3200-2800 cm^{-1} possessing the characteristic features of methylene group[5] partially overlapped with N-H stretching vibration particularly on the higher frequency band, i.e., 3200 cm^{-1}. There is no evidence of any S–H band in the region 2600-2400 cm^{-1}.

In the region 1750-1600 cm^{-1} of the ligand spectrum there appeared two strong bands, one at about 1720 cm^{-1} and another ~1600 cm^{-1}. These bands most probably arise respectively due to C=O and C=N (acyclic) stretching vibrations[6-8] of structure II. The C=O band of the ligand practically remains unaffected in the metal complexes[9]. On the other hand, C=N stretch undergoes a shift towards lower frequency region due to coordination with metal ions in almost all the metal complexes.

Other important vibrational bands in the ligand and the metal complexes are observed near 1350, 1240, 1200, 1140 and 900 cm^{-1} respectively. These bands do not seem to be much affected on coordination. Another band at 800 cm^{-1} which most probably arises due to C–S stretching vibration remains almost unperturbed in the metal complexes, implying that the S atom of the ring does not participate in coordination with the metal ions. Logically these observations lead us to suggest that the most probable structure of the metal complexes are as shown in Fig. III.



III

TABLE 1—ANALYTICAL DATA OF *bis*-2(IMINO)-4-THIAZOLIDINONE AND ITS METAL CHELATES

Sl. No.	Formula	Colour	μ_{eff} in B.M. at 26°±1°C	Metal% Found (Calcd.)	Sulphur% Found (Calcd.)	Nitrogen% Found (Calcd.)
	(H_2BITZ)	White			27.58 (27.60)	24.09 (24.34)
2.	Cu(BITZ)	Green	1.72	21.65 (21.79)	21.86 (21.96)	21.86 (19.22)
3.	Ni(BITZ)	Green	3.28	20.38 (20.46)	22.35 (22.32)	19.25 (19.53)
4.	Co(BITZ)	Chocolate	3.80	20.50 (20.52)	22.28 (22.30)	19.07 (19.53)
5.	Fe(BITZ), $3H_2O$	Chocolate	3.54	16.32 (16.54)	18.78 (18.94)	16.28 (16.58)
6.	Mn(BITZ)	Light-green	5.50	19.38 (19.41)	22.55 (22.62)	19.48 (19.80)
7.	Pd(BITZ), $3H_2O$	Brick-red	Diamagnetic	27.22 (27.39)	16.50 (16.47)	14.60 (14.42)
8.	Zn(BITZ)	White		22.21 (22.29)	21.45 (21.81)	18.78 (19.08)
9.	Cd(BITZ)	White		32.98 (33.01)	18.73 (18.80)	16.32 (16.45)
10.	Hg(BITZ)	Light-yellow		46.75 (46.80)	14.85 (14.94)	13.25 (13.07)
11.	Mg(BITZ), $4H_2O$	White		9.03 (9.42)	19.45 (19.78)	16.96 (17.27)

The bands in the electronic spectra of the ligand ~46,000 cm^{-1} to 45,000 cm^{-1} and 40,000 cm^{-1} to 37,000 cm^{-1} may be either due to $n\rightarrow\sigma^*$ or $n\rightarrow\pi^*$ transitions.

The Cu(II), Ni(II), Co(II) and Mn(II) complexes are paramagnetic (Table 1) whereas the Pd(II) complex is diamagnetic. The visible absorption bands of the copper(II) complex at ~14,000 and 20,000 cm^{-1} may be assigned to $(^2A_{1g}\approx{}^2B_{2g})\rightarrow{}^2E_g$ and $^2B_{2g}$ transitions. The charge-transfer band appears ~25,000 cm^{-1}. The spectrum of Ni(II) complex shows three ligand field bands at 15,500, 20,000 and 26,000 cm^{-1}. The first band corresponds to $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ while the last to $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ transitions respectively.

The electronic spectra of cobalt(II) complex show a band system in the region 16,000 to 19,000 cm^{-1} which possesses the characteristic features of the electronic spectra of known octahedral complexes. The band may be assigned to $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ transition in an approximately octahedral field. The observed magnetic moment of the complex (3.80 B.M.) is lower than the value expected for spin-free complex. This may be due to two types of ions, i.e., spin-free and spin paired cobalt(II) ions. Nandi and Ghosh[10] have reported several cobalt(II) complexes which possess low magnetic moments, i.e., 3.75 to 3.92 B.M. However, no definite explanation can be given here. The chelates probably possess polymeric structure wherein the ligand acts in a bi-bifunctional manner spanning towards two metal ions in *trans* positions and giving rise to the chromophore MN_4. The octahedral field may be due to intermolecular out of plane coordination.

Acknowledgement

Grateful thanks are due to Sambalpur University and C.S.I.R., New Delhi for the Junior Research Fellowship awarded to (T.D.M.) and (H.P.M.) respectively.

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J. INDIAN CHEM. SOC., VOL. LVII, DECEMBER 1980

Metal Complexes of 3-3′ (*bis*)-Thiohydantoin with Bivalent Metal Ions

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Manuscript received 3 December 1979, revised 27 May 1980, accepted 9 September 1980

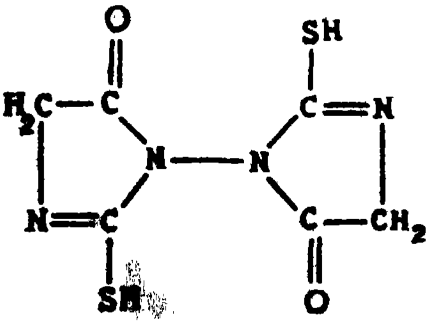
THE preparation of metal chelates with N,N′-di (thiocarbamoyl) hydrazine has been reported by us earlier[1]. 3-3′ (*bis*)-thiohydantoin (H_2BTHT) is a derivative of N,N′-di (thiocarbamoyl) hydrazine[2]. As a part of our programme to study the fungitoxicity of sulphur donor ligands and their metal complexes, attempts were made to synthesize metal chelates with H_2BTHT.

Experimental

3-3′ (*bis*)-thiohydantoin (H_2BTHT) was prepared by literature method[2] (m.p. 260°). Metal complexes were prepared adopting standard procedure[3]. The constituent parts of each complex have been estimated by established analytical methods[4]. The i.r. spectra, electronic spectra and magnetic susceptibility measurements were carried out as reported earlier[3].

Results and Discussion

A striking feature in the i.r. spectra of the component reactant, N,N′-di (thiocarbamoyl) hydrazine[1] is the appearance of a series of bands in the vicinity of 3300 cm^{-1} which arise due to the stretching vibrations of NH_2 and NH groups. Another significant band of strong intensity and of moderate width appears near 1545 cm^{-1} which arises due to NH_2 deformation. All these bands are significantly absent in the newly synthesized organic molecule and clearly imply the non-existence of either NH_2 or NH or OH groups and provide strong evidence in favour of the existence of the compound in structural form I. The S-H stretching vibrations[5] appearing as a weak band in the ligand ~2460 cm^{-1} disappear in the inner complex salts.



I

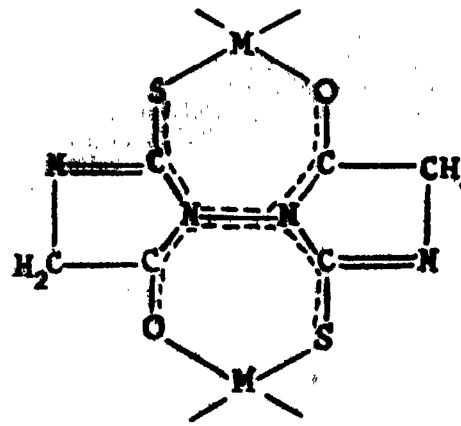
In the region 3600-3200 cm^{-1} a strong and broad band appears in all the metal complexes that contain water of hydration. The high frequency band observed at 1730 cm^{-1} in the ligand attributed to C=O stretching vibration undergoes a shift to a lower frequency region (40-50 cm^{-1}) in all the metal complexes[3]. The C=N band (at 1625 cm^{-1}) on the other hand is found to shift to a higher frequency region or remains nearly unaffected.

A relatively broad band of medium intensity appears in the spectra of the ligand near about 1400 cm^{-1} which shows considerable structure and most probably arises due to CH_2 deformation and C=S stretching vibrations[6-9]. In the metal complexes there appear a much sharper band at ~1400 cm^{-1} and an additional band of medium intensity appears near 1300 cm^{-1}. These observations indicate the shift of the ligand C=S stretching vibration (observed at 1400 cm^{-1}) towards a lower frequency region, keeping the CH_2 deformation vibration unaffected and further attribute the coordination of C=S group with the metal ions.

Two ligand bands at about 1350 cm^{-1} and 1250 cm^{-1} do not undergo much change in the metal complexes and probably arise due to CH_2 deformation vibrations.

The characteristic ν(C=S) in the lower frequency region[10,11] is reported in the range 805-720 cm^{-1}. The ligand band appearing at 720 cm^{-1} may be attributed to ν(C=S) vibration which undergoes a downward shift in all the metal complexes.

These observations logically lead us to propose the structure of the metal complexes as shown in Fig. II wherein the ligand is bonded to the metal ions in a tetrafunctional manner involving coordination of C=O and C=S groups and spanning towards two metal ions in *trans* structures and further forming delocalized seven-membered chelate ring.



II

TABLE 1—ANALYTICAL DATA OF 3-3'(*bis*)-THIOHYDANTOIN AND ITS METAL CHELATES

Sl. No.	Formula	Colour	Metal% Found (Calcd.)	Sulphur% Found (Calcd.)	Nitrogen% Found (Calcd.)	μ_{eff} in B.M. at 32°±1°C
1.	(H_2BTHT)	White		27.78 (27.83)	24.40 (24.35)	
2.	Cu(BTHT), $2H_2O$	Green	19.24 (19.89)	19.98 (19.54)	17.02 (17.10)	1.75
3.	Ni(BTHT), H_2O	Light-green	19.28 (19.26)	21.23 (21.00)	18.47 (18.83)	2.46
4.	Co(BTHT), H_2O	Brown	19.38 (19.32)	20.98 (20.99)	18.27 (18.87)	4.31
5.	Fe(BTHT), $2.5H_2O$	Pale green	16.96 (16.99)	19.28 (19.45)	16.98 (17.02)	5.44
6.	Mn(BTHT), $2H_2O$	Grey	17.98 (17.16)	20.23 (20.01)	17.45 (17.51)	5.89
7.	Pd(BTHT), $3H_2O$	Chocolate	26.92 (27.39)	16.32 (16.47)	14.60 (14.42)	Diamagnetic
8.	Cd(BTHT), $3H_2O$	White	28.93 (28.56)	16.19 (16.23)	13.75 (13.88)	
9.	Hg(BTHT), H_2O	Light-yellow	44.48 (44.91)	12.95 (12.54)	14.79 (14.33)	
10.	Mg(BTHT), $4H_2O$	White	9.32 (9.44)	19.55 (19.73)	17.02 (17.27)	

The electronic spectra of copper(II) complex show an asymmetric ligand field band in the region 14,000-17,000 cm^{-1} which can be assigned to $(^2A_{1g}\approx{}^2B_{2g})\rightarrow{}^2E_g$ and $^2B_{2g}$ transition[12] under a tetragonal field. The chromophone CuS_2O_2 may be considered to have D_{2h} symmetry. Important transition is observed in the spectrum of Ni(II) complex at 16,000 cm^{-1}. This band may be assigned to $^3A_{2g}\rightarrow{}^3G_{1g}$ (F) transition under octahedral approximation. The charge transfer band has been assigned beyond 20,000 cm^{-1}. Cobalt(II) complex shows a band system in the region 16,000-20,000 cm^{-1} which may be assigned to $^4T_{1g}$ (F)$\rightarrow{}^4T_{1g}$ (P) transition in an approximately octahedral field. Paramagnetism has been noticed in the complexes of Cu(II), Ni(II), Co(II) and Mn(II). The Pd(II) complex is diamagnetic.

Cobalt(II) complex exhibits low magnetic moment. This may be due to the presence of two types of species i.e., spin-free and spin-paired ions as reported earlier[13].

High insolubility of the complexes in water and in common organic solvents point towards polymeric structure. The octahedral field may be due to out of plane coordination through S atom.

Acknowledgement

The authors are thankful to C.S.I.R., New Delhi and Sambalpur University for the award of Junior Research Fellowships to (H.P.M.) and (T.D.M.) respectively.

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Electronic Spectra of Mixed Halocobaltates (II) in Acetonitrile and Nitromethane

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Manuscript received 4 February 1980, revised 5 August 1980, accepted 9 September 1980

A few mixed trihalo-, tetrahalo- and pentahalocobaltates(II) have been isolated and characterized by us [1-3] and their electronic spectral study in nujol mull has also been reported[4,5]. Now we are reporting the solution spectra of mixed tetra- and pentahalocobaltates(II).

Experimental

The mixed tetra- and pentahalocobaltates(II) were prepared according to the methods reported earlier [2,3]. A Unicam SP700 spectrophotometer was used for recording the spectra in visible and near i. r. regions in acetonitrile and nitromethane solutions. BDH grade acetonitrile was purified by the method of Walden and Birr[6] which consisted in repeated distillation over phosphorus pentaoxide till the dehydrating agent no longer turned yellow, followed by distillation over anhydrous potassium carbonate to remove traces of P_2O_5 and final distillation without any drying agent. BDH grade nitromethane was purified by drying P_2O_5 and fractional distillation, the fraction distilled at 101° was collected.

1 cm matched silica cells were used to hold the solution and solvent. Higher concentrations had to be used for recording the spectrum in the near i. r. region than in the visible region. For comparison purpose diffuse reflectance spectra of these compounds were also recorded using MgO as reference.

Results and Discussion

Mixed Tetrahalo Cobaltates(II) : It has been observed that the effect of low symmetry in the case of mixed tetrahalocobaltates(II) [C_{2v} for $(CoX_2Y_2)^{2-}$] as compared to simple tetrahalocobaltates(II) (Td for CoX_4^{2-}) on the electronic spectra (in nujol mull) is not significant and, in fact, ligand field parameters for the former have been calculated using equations applicable to tetrahedral symmetry[5].

The centres of gravity of ν_3 bands in acetonitrile, nitromethane and diffuse reflectance and of ν_2 bands in acetonitrile** are reported in Table 1 and are two representative spectra in the visible region are shown in Fig. 1. It is clear from the

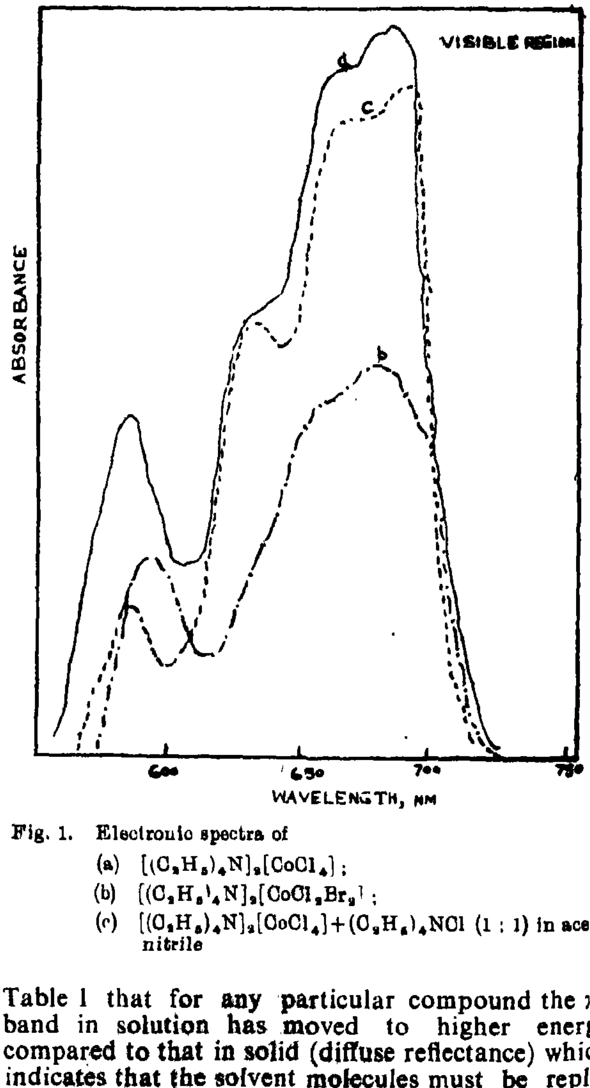


Fig. 1. Electronic spectra of
(a) $[(C_2H_5)_4N]_2[CoCl_4]$;
(b) $[(C_2H_5)_4N]_2[CoCl_2Br_2]$;
(c) $[(C_2H_5)_4N]_2[CoCl_4]+(C_2H_5)_4NCl$ (1 : 1) in acetonitrile

Table 1 that for any particular compound the ν_3 band in solution has moved to higher energy compared to that in solid (diffuse reflectance) which indicates that the solvent molecules must be replacing one or more halides from the coordination sphere, thus still retaining the tetrahedral geometry but moving the band to higher energy side due to higher position of the solvent molecule in the spectrochemical series. The hypothesis of solvent coordination was confirmed by the observation of red shift in the ν_3 and ν_2 bands of a mixture of $(C_2H_5)_4N_2CoCl_4$ and $(C_2H_5)_4$ NCl in acetonitrile as compared to those of $[(C_2H_5)_4N]_2$ $CoCl_4$ alone (Table 1).

A peculiar phenomenon in the acetonitrile solution spectra is that while ν_3 values are in the

* Correspondence to be addressed to.

** ν_2 bands could not be recorded in full in nitromethane and diffuse reflectance.

Table 1—γ_3 and γ_2 Transitions in Halocobaltates(II)

$B=(nC_4H_9)_4N^+$; $E=(C_2H_5)_4N^+$; $M=(CH_3)_4N^+$

Compound	γ_3(cm^{-1}) (Acetonitrile)	γ_2(cm^{-1}) (Acetonitrile)	γ_3(cm^{-1}) Reflectance	γ_3(cm^{-1}) (CH_3NO_2)
$M_2(CoCl_4)$	15385	5236	15150	15267
$E_2(CoCl_4)$	15814	5263	—	15150
$E_2(CoCl_2Br_2)$	15198	5848	14749	15106
$E_2(CoCl_2I_2)$	14970	5464	14888	14925
$E_2(CoBr_2I_2)$	14585	5495	13889	15106
$M_2(CoBr_4)$	14815	5291	14493	14815
$M_3(CoCl_5)$	15270	5291	15267	15267
$E_3(CoCl_5)$	15150	5208	15198	15106
$E_3(CoCl_4Br)$	15840	5291	14925	—
$E_3(CoCl_3Br_2)$	15270	5291	14815	15198
$M_3(CoCl_2.Br_3)$	15150	5376	14993	15106
$E_3(CoCl_2.Br_3)$	15040	5848	14641	15038
$M_3(CoCl_2.Br_3)$	15840	5361	14641	15038
$E_3(CoCl.Br_4)$	15200	5848	14706	15150
$M_3(CoBr_5)$	14815	5291	14600	14706
$B_2(CoCl_2I_2)$*	15200	—	14430	15198
$B_2(CoBr_2I_2)$*	14600	—	13986	14600
Equimolecular Mixture of $E_2(CoCl_4)+ECl$	15150	5208	—	15106

* γ_2 bands were not observed fully.

expected order, that is, $Cl^- > Br^- > I^-$, γ_2 values are reverse of the expected order (Table 1); this may be attributed to high absorption by the solvent in the near i. r. region or possibly the solvent interacts with the complex ion in some other way than simple coordination.

Mixed Pentahalocobaltates(II) : We have concluded from the electronic spectral (nujol mull) and far i. r. studies[3] that the mixed pentahalocobaltates(II), in fact, are double salts containing tetrahedral cobalt e. g., $(CoCl_4Br)^{3-}$ is $(CoCl_3Br)^{2-}Cl^-$. The solution is similar to that in Cs_3CoCl_5 which has been shown to be $Cs_2CoCl_4.CsCl$ by crystallography[8]. The γ_3 values for the mixed pentahalocobaltates(II) are nearly the same as for the corresponding mixed tetrahalocobaltates(II) and they also show a similar trend (Table 1). This supports the assumption that similar ions are present in the solution of both the halocobaltates(II).

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Preparation and Characterisation of µ-Dihydroxotetrakis(Salicylato)-Diaquodichromium(III)

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Manuscript received 3 May 1980, revised 4 August 1980, accepted 9 September 1980

Gillard[1] and coworkers have studied oxidative degradation mechanism of coordinated salicylic acid in form of *bis*(ethylenediamine)salicylatocobalt(III) and have reported that the reactivity of salicylate is markedly modified by coordination. Complexes of cobalt(III) containing the bidentate salicylate ion undergoes reaction in which the organic moiety is modified while remaining bound to the metal ion. While trying to extend the study to other salicylate complexes, it was found that the salicylate complexes of many metals including those of transition metals have been reported by a number of workers[2-5] but most of these studies have been carried out in solution. In this paper we report the preparation and characterisation of µ-dihydroxotetrakis(salicylato)diaquodichromium(III) by analysis, derivatographic study, i.r. spectra, magnetic susceptibility measurements, U.V. and visible reflectance spectra. Lastly the oxidation of the complex was carried out in 12 *N* sulphuric acid medium.

The instruments used and method of preparation of the complex have been described earlier[6,7]. The percentages of chromium were determined volumetrically[8]. C and H were estimated by element estimation technique. Complete analysis gives (Found Cr = 14.2%, C = 45.9%, H = 3.9%, calculated for $[Cr_2(OH)_2(OHC_6H_4COO)_4(H_2O)_2]$ Cr = 14.4%, C = 46.45% and H = 3.7%. The stages of oxidation were followed potentiometrically[9] using bright platinum electrode on a Chrompton potentiometer. The concentrations were so chosen that 10 ml of M/1120 µ-dihydroxotetrakis (salicylato) diaquodichromium(III) requires 10 ml of M/60 $K_2Cr_2O_7$ for complete oxidation to CO_2 stage.

Derivatographic Study :

The combined D.T.G., D.T.A. and T.G.A. curve of a sample of 500 mg of the complex µ-dihydroxotetrakis(salicylato)diaquodichromium(III) was carried out with heating rate of 8°/min. The temperature was fixed between 30° to 800°. The summary of the results is tabulated in Table.

The first three products were confirmed by i.r. spectra, chemical tests and element estimation technique. The metal carbonate was confirmed by chemical tests and quantitative liberation of Co_2. The final product was confirmed by powder X-ray analysis.

TABLE

D.T.G. curve reading (in °C)	The compound formed and the loss in weight in T.G.A. curve		Nature inflexion point of the peak in D.T.A. curve in °C
60-140	$[Cr_2(OH)_2(OHC_6H_4COO)_4]$	24mg	Endo at 180
150-240	$[O\{Cr_2(OHC_6H_4COO)_4\}]$	87mg	Endo at 240
240-310	$[O\{Cr_2(OC_6H_4COO)_2\}]$	237mg	Endo at 270
310-470	$[Cr_2O(CO_3)_2]$	331mg	Exo at 360 Endo at 460
470-600	Cr_2O_3	391mg	Exo at 550 Endo at 600

Endo = Endothermal peak, Exo = Exothermal peak.

I. R. Spectra, Magnetic, U. V. and Visible Reflectance Spectra :

The i.r. spectra of the complex was carried out in nujol mull, magnetic and reflectance spectra were taken in solid phase at room temperature. The i.r. spectrum of the complex $[Cr_2(OH)_2(OHC_6H_4COO)_4(H_2O)_2]$ exhibits a strong and broad band at 3450 cm^{-1} and a sharp band at 960 cm^{-1} attributed to bridged hydroxyl group in the complex[10]. The broadening of $\nu(C=O)$ vibration at 1595 cm^{-1} and splitting of $\nu(C-O)$ vibrations into two bands 1370 cm^{-1} and 1308 cm^{-1} indicates that some of the salicylic acid molecules are coordinated to Cr(III) atoms through both the carboxylic and phenolic oxygen while the rest are monocoordinated. The medium bands at 1620 cm^{-1} and 808 cm^{-1} are attributed to coordinated water molecules.

The magnetic moment value of the complex was found to be 3.45 B.M. The electronic reflectance spectra exhibit two bands at 16390 cm^{-1} and 23810 cm^{-1} assignable to $^4A_{2g} \rightarrow ^4T_{2g(F)}$ and $^4A_{2g} \rightarrow ^4T_{1g(F)}$ transitions respectively in octahedral ligand field. The lower magnetic value[11] and 10 Dq value[12,13] in the present case might be due to bridged nature of weak ligand field energy of salicylato group.

Oxidation :

The very sharp inflexion obtained at 3.8 ml after 3 hrs storage at room temperature corresponding to 10 electron abstraction stage per molecule of salicylic acid and the i.r. spectra indicate the destruction of aromatic ring. The intermediate stage could not be identified. At 12 hrs storage at room temperature a very sharp inflexion point was obtained at 5.0 ml. i.e., 14 electron abstraction per salicylic acid molecule. The products obtained at this stage were characterised as *bis*(maleato)diaquochromium(III) and *bis*(oxalato)diaquochromium(III) complex as intermediate products spectrophotometrically and by paper chromatography. On prolonged storage at room temperature (240 hrs) inflexion point was obtained at 7.8 ml corresponding to 22 electron abstraction. The oxidation product of coordinated salicylate was identified to be predominantly *cis-bis*(oxalato)diaquochromium(III). The complete oxidation of coordinated salicylate to carbon dioxide and water takes place only after heating at 90° for 18 hrs.

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Synthesis of 5-Hydroxy-3', 4', 5', 7-Tetramethoxy-8-Prenylflavanone

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Manuscript received 5 July 1979, revised 16 September 1980, accepted 29 October 1980

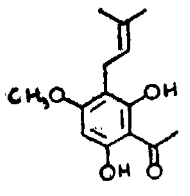
5-HYDROXY-3', 4', 5', 7-tetramethoxy-8-prenylflavanone has been synthesised by a new route, involving lesser number of steps and in better yield, starting from 4-*o*-methylphloroacetophenone[1] which on prenylation gave two compounds, identified as 4-*o*-methyl-3-prenylphloroacetophenone(I) and gem-di-C-prenyl-4-*o*-methylphloroacetophenone(II) on the basis of spectral data. Ketone (I) on condensation with 3, 4, 5-trimethoxybenzaldehyde[2] under alkaline conditions gave the title compound (III) which agreed in its characteristics with the sample prepared earlier[3] by a different route. Methylation of III yielded IV which was also made from the corresponding chalcone[4](V).

Experimental

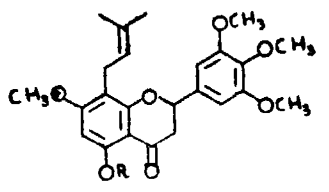
Prenylation of 4-o-methylphloroacetophenone :

To an ice cold solution of 4-*o*-methylphloroacetophenone (5 g) in alcoholic KOH (3g in 50 ml)

was added prenyl bromide (5 g) and the reaction mixture stirred for 24 hr at room temperature. Work up of the product followed by column chromatography over silica gel using petroleum ether-benzene mixture gave ketones(I) and (II), with the latter coming out first.

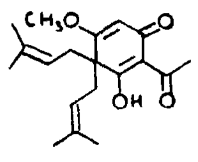


I

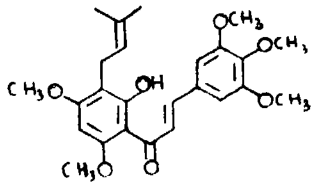


III ; R = H

IV ; R = CH_3



II



V

I : (3-Prenyl-4-*o*-methylphloroacetophenone), yellow needles ; m. p. 125-6° ; dark brown ferric reaction ; ν_{max}^{KBr} 1635 cm^{-1} ; λ_{max}^{MeOH} : 290, 325 (3.91, 3.12) nm ; NMR (δ, $CDCl_3$) : 1.8 (s, 6H, gem dimethyl), 2.69 (s, 3H, $-COCH_3$), 3.3(d, J=7Hz, 2H, $ArCH_2-$), 3.9 (s, 3H, $-OCH_3$), 5.15 (m, 1H, olefinic proton), 5.98 (s, 1H, aromatic proton), 9.2 (s, 1H, C_2-OH), 11.4 (s, 1H, C_6-OH). (Found : C, 67.0 ; H, 7.5. $C_{14}H_{18}O_4$ requires C, 67.2 ; 7.25%).

II : (Gem-di-C-prenyl-4-*o*-methylphloroacetophenone), colourless plates ; m.p. 68° ; orange-red ferric reaction ; ν_{max}^{KBr} 1650-1400 (br), 1215 cm^{-1} ; λ_{max}^{MeOH} : 260, 270, 310 (4.02, 4.02, 4.32) nm ; NMR (δ, $CDCl_3$) : 1.55 (s, 12H, four methyl of two prenyl groups), 2.45-2.75 (m, 7H, $-COCH_3$ & $2\times ArCH_2-$), 3.75 (s, 3H, $-OCH_3$), 4.75 (t, 2H, olefinic protons of two prenyl groups), 5.5 (s, 1H, ring proton), 18.4 (s, 1H, D_2O exchanged, $-OH$). (Found : C, 71.9 ; H, 8.3. $C_{19}H_{26}O_4$ requires C, 71.7 ; H, 8.17%).

5-Hydroxy-3', 4', 5', 7-tetramethoxy-8-prenylflavanone(III) :

To an ice cold solution of I (400 mg) in 20 ml of 25% alcoholic KOH was added 3, 4, 5-trimethoxybenzaldehyde (360 mg) and the mixture was kept at 0° for 24 hr. The product, which was found to be a mixture of a flavanone and the unreacted ketone, was subjected to preparative TLC over silica gel using benzene-acetone (9 : 1) as developing solvent. The flavanone crystallised from alcohol as colourless needles ; m. p. 150-51° (lit[3] m. p. 150-51°) ; green ferric reaction and negative Gibbs test ; ν_{max}^{KBr} 1625 cm^{-1}, λ_{max}^{MeOH} : 290, 335 (4.10, 3.50) ; with $AlCl_3$, 315, 365 ; with $AlCl_3$+HCl, 315, 365, with NaOMe, 290, 360 nm ; NMR (δ, $CDCl_3$) 1.65 (s, 6H, gem dimethyl), 2.95 (m, 2H, H−3), 3.25 (d, J=7Hz, 2H, $ArCH_2-$), 3.9 (s, 12H, $4\times -OCH_3$), 5.3 (m, 2H, H-2 and olefinic proton of prenyl group), 6.14 (s, 1H, H-6), 6.73 (s, 2H, H−2' & 6'), 12.10 (s, 1H, OH). (Found : C, 67.1 ; H, 7.0. $C_{24}H_{28}O_7$ requires C, 67.3 ; H, 6.59%).

5,7,3',4',5'-Pentamethoxy-8-prenylflavanone (IV) :

(a) To a solution of flavanone(III, 40 mg) in dry acetone (5 ml) was added anhydrous K_2CO_3 (1 g) and dimethylsulphate (0.2 ml).

The mixture was refluxed for 5 hr. The product obtained after standard workup was purified by preparative TLC. It gave colourless needless ; m.p. 170-71° ; negative ferric reaction ; ν_{max}^{KBr} 1660 cm^{-1} ; λ_{max}^{MeOH} : 290, 320 nm ; NMR (δ, $CDCl_3$) : 1.65 (s, 6H, gem dimethyl), 2.9 (m, 2H, H−3), 3.3 (m, 2H, $ArCH_2$), 4.1 (s, 9H, $3\times -OCH_3$), 4.15 (s, 3H, OCH_3), 4.2 (s, 3H, $-OCH_3$), 5.5 (m, 2H, H−2 & olefinic proton), 6.15 (s, 1H, H−6), 6.7 (s, 2H, H−2' & 6'). (Found : C, 67.6 ; H, 7.2. $C_{25}H_{30}O_7$ requires C, 67.8 ; H, 6.9%).

(b) The chalcone[4] (V, 50 mg) was cyclised, by heating with pyridine (1 ml) and piperidine (1 ml) at 60° for 11 hr, into a flavanone which was found to be identical with IV in all respects (co-TLC, mmp, superimposable IR).

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Synthesis, Characterization and Screening of Antibacterial Activity of Some New Mannich Bases

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Manuscript received 7 May 1979, revised 7 April 1980, accepted 26 July 1980

THE use of Mannich bases as analgesic[1], anti-bacterial[2] and anti-inflammatory[3] compounds encouraged us to synthesize some new Mannich bases. A survey of literature reveals that Ram and Pandey[4] have synthesized a number of Mannich bases from 5-substituted-1, 3, 4-oxadiazol-2-thione and its derivatives and from 3-methyl-isooxazolin-5-one. Singh, Bindal and Dixit[5] prepared these bases from isovaleramide. Werner and Walter[6] prepared Mannich bases by treating 2-hydroxy-4-methoxy-acetophenone with formaldehyde and dimethyl-amine. But Mannich bases have not yet been synthesized from resacetophenone, 2,5-dihydroxy-acetophenone, gallacetophenone, pholoroacetophe-none, 2-acetylbenzofuran, *p*-phenylacetophenone and 3-acetyl-4-hydroxycoumarin. So the authors thought to synthesize Mannich bases from these substituted ketones and to test the antibacterial activity of some of these bases.

Experimental

IR spectra were recorded in KBr pellets using Beckmann spectrophotometer. All the m.p. are uncorrected and taken in open capillary.

General Procedure for the Synthesis of Mannich Bases :

To a cold ethanolic (95 %) solution of ketone (0.02 mole), formaldehyde (2 ml, 40%) was added and left in ice-mix. for a few minutes. To the cold mix. an amine (0.02 mole) solution in ethanol was added dropwise and with constant stirring and left in ice-mixture with occasional stirring. The time of formation of each base was recorded carefully. The Mannich bases were filtered, washed with distilled water and a little ethanol and recrystallized from a suitable solvent (Table 1).

Resacetophenone[7], 2,5-dihydroxyacetophenone[8], gallacetophenone[9], phloroacetophenone[10], *p*-phenyl-acetophenone[11] and 3-acetyl-4-hydroxycoumarin[12] used in the synthesis of Mannich bases were pre-pared from literature methods.

In the infra-red spectrum a broad absorption band was observed in the region 3400-3550 cm^{-1} suggesting the presence of an intramolecular hydro-gen bonded hydroxyl group in the bases. A sharp absorption band in the region 1660-1700 cm^{-1} indi-cates ν(C=O). The weak absorption band observed

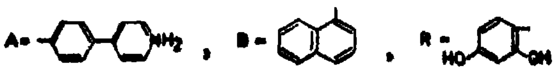
TABLE 1—MANNICH BASES OF ARYL KETONES

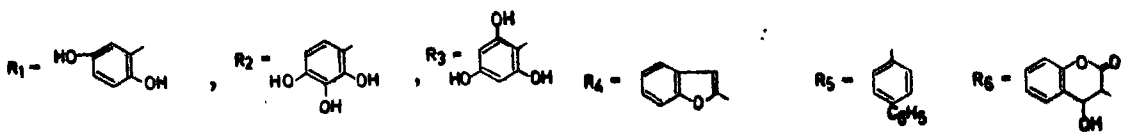
Sl. No.	Name of the compounds	Time of formation (hr)	Recrystallising solvents	m.p. (°C)	Structure formula	Diameter of zone (mm)	Average
1.	β-Phenylamino-2 : 4 D.P.	1	acetone	135	$RCOCH_2CH_2$ | Ph—NH	13.4, 14.1, 14.3, 14.8, 13.6, 14.0, 14.2, 13.8.	14.02 mm
2.	β-Benzidinyl-2 : 4 D.P.	2½ – 3	aq. ethanol	149	$RCOCH_2CH_2$ | A—NH	12.3, 12.0, 11.8, 12.8, 12.2, 12.8, 13.0, 12.0.	12.30 mm
3.	β-Diphenylamino-2 : 4 D.P.	24	ether solvent	90	$RCOCH_2-CH_2$ | Ph₂>N		
4.	β-Phenylamino-2 : 5 D.P.	1	ethanol	235	$R_1COCH_2-CH_2$ | Ph—NH	15.5, 15.0, 15.0, 14.3, 14.0, 14.2, 14.0,	14.55 mm
5.	β-Benzidinyl-2 : 5 D.P.	½	aq. ethanol	140	$R_1COCH_2-CH_2$ | A—NH	16.4, 17.2, 16.4, 16.0, 16.2, 16.0, 16.5, 16.6.	16.41 mm
6.	β-Benzidinyl-2,3,4 T.P.	½	acetone	180	$R_2COCH_2-CH_2$ | A—NH		
7.	β-(α)-Naphthyl-amino-2,3,4 T.P.	3½	aq. ethanol	167	$R_2COCH_2-CH_2$ | NH | B	22.0, 21.6, 22.0, 22.2, 21.8, 22.0, 21.8, 22.0.	21.92 mm
8.	β-Benzidinyl-2,4,6-T.P.	½	ethanol	above 320	$R_3COCH_2-CH_2$ | A—NH		

* For correspondence.

(Table 1 Contd.)

9.	β-(α)-Naphthyl-amino-2,4,6 T.P.	2	ethanol	above 320	$R_3COCH_2-CH_2$ │ NH │ B		
10.	2-(β)-Phenylamino-propionyl benzofuran	1	acetone	184	$R_4COCH_2-CH_2$ │ Ph—NH		
11.	β-Benzidinyl-(p)-phenyl P.	½	aq. ethanol	147	$R_5COCH_2CH_2$ │ A—NH		
12.	β-(α)-Naphthyl-amino-(p)-phenyl P.	1½	acetone	185	$R_5COCH_2CH_2$ │ B—NH	21.0, 21.0, 21.8, 21.8, 20.8, 20.7.	21.18 mm
13.	3-(β)-Phenylamino propionyl-4-hydroxy-coumarin	1	ethanol	165	$R_6COCH_2CH_2$ │ Ph—NH		

D=*Dihydroxy*, *T*=*Trihydroxy*, P=*Propiophenone*, *Ph*=*Phenyl*, 



in the region 3300-3350 cm^{-1} is characteristic of $\nu(-NH)$.

The N.M.R. spectrum of the Mannich bases in $CDCl_3$ shows a multiplet from 6.88 δ to 7.48 δ and a sharp singlet at 4.69 δ indicating the presence of the aromatic and methylene protons, respectively. The absorption of amino proton is observed at 3.30 δ.

Screening for Antibacterial Activity :

The compounds 1, 2, 4, 5, 7 and 12 listed in Table 1 were screened for their inhibitory effects against two organisms viz., *Bacillus cereus* (Gram positive) and *Escherichia coli* (Gram negative) by agar diffusion technique[13] and the results obtained are depicted in Table 1. The concentration of the soln. was 0.5 mg/ml in D.M.F. The bases were found to exhibit activity against *Bacillus cereus* only. Bacterial cultures were maintained at Microbiology Department of Central Pharmaceutical Laboratory, New Rajnagar, Ghaziabad.

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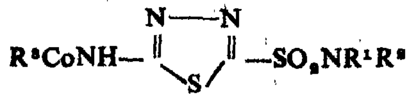
New 5-Arylamino-2[N-(2'-Mercaptoacetylamino-4'-Arylthiazolo)]-Thiadiazoles(III) : as AChE Inhibitors

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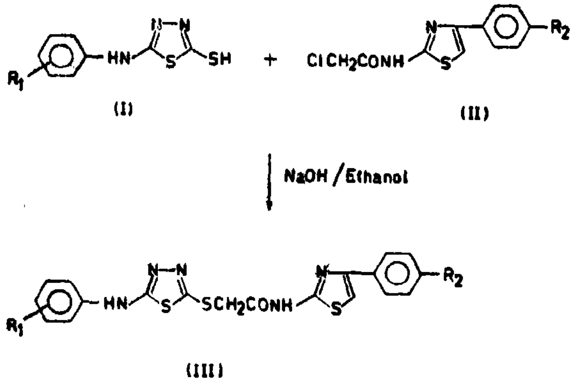
Manuscript received 27 November 1979, revised 30 May 1980, accepted 7 August 1980

THIADIAZOLES are known as potent fungicide[1], insecticide[2] and bactericide[3]. 5-Acylamino-1,3,4-thiadiazol-2-sulfonamide, an efficient pre- and postemergent herbicide has been reported by Kirkpatrich[4].



It is well known that sulfur containing compounds affect their toxic action by inhibition of acetylcholinesterase which exhibit physiological significance in the nervous system[5]. Authors, therefore synthesised the title compounds with a view to study their inhibitory properties against cholinesterase.

5-Arylamino-2-mercapto-1, 3, 4-thiadiazoles(I) on condensation with 2-chloroacetylamino-4-arylthiazoles(II), afforded the 5-arylamino-2[N-(2'-mercaptoacetylamino - 4-arylthiazolo)]-thiadiazoles (III) in ethanol solution. These compounds showed strong peaks at 3280 (NH-stretching), 1680 (C=O) ; 1550 (cyclic C=N) ; 1340 (pentacyclic ring) ; 1260 (N−N=C) ; 830 (disubstituted benzene ring).



Experimental

Melting points were taken in open capillary tubes and are uncorrected. The synthesised compounds were satisfactorily characterised by IR, elemental analyses and TLC.

The 5-arylamino-2-mercapto-1,3,4-thiadiazole[6](I) and 2-amino-4-arylthiazole[7] have been prepared by known procedures. Chloroacetylation of the latter yielded 2-chloroacetylamino-4-aryl-thiazole(II).

5-(4-Ethoxyphenylamino)-2-[N-(2'-mercaptoacetylamino-4'-chlorophenylthiazolo)]-thiadiazole(III) :

A mixture of 0.40 g (0.01 mole) sodium hydroxide and 2.53 g (0.01 mole) 5-(4-ethoxyphenylamino)-2-mercapto-1, 3, 4-thiadiazole was heated under reflux for 30 mnts. 2.88 g (0.01 mole) 2-chloroacetylamino-4-chlorophenyl thiazole was added to the above solution and refluxed for additional 4 hours. The reaction mixture was poured in ice cold water. The solid mass thus separated was filtered and crystallised from ethylalcohol (Table 1).

TABLE 1—5-ARYLAMINO-2[N-(2'-MERCAPTOACETYLAMINO-4'-ARYLTHIAZOLO)]-THIADIAZOLES(III)

Sl. No.	R_1	R_2	m.p. °C	Yield
1.	4-CH_3	H	229	67
2.	H	H	236	62
3.	4-OC_2H_5	H	236	60
4.	4-Cl	H	215	65
5.	2-OCH_3	H	222	55
6.	4-Br	H	234	58
7.	4-CH_3	Cl	233	60
8.	H	Cl	230	60
9.	4-OC_2H_5	Cl	231	57
10.	4-Cl	Cl	202	62
11.	2-OCH_3	Cl	228	55
12.	4-Br	Cl	231	57

Determination of Antiacetylcholinesterase activity :

Method of Colowick *et al*[8] has been employed to determine the enzyme inhibition which is a modification of Hestrin's[9] procedure. Compounds were dissolved in propylene glycol and were used at a concentration of $3.8\times10^{-4}M$. A control containing equal volume of propylene glycol was also run in parallel. All the tested compounds showed considerable inhibition. Neostigmine, a potent AChE inhibitor has been used as standard in similar conditions having I_{50} value 1.96×10^{-7}. I_{50} value denotes the concentration required for 50% enzyme inhibition.

TABLE 2—ANTIACETYLCHOLINESTERASE ACTIVITY OF 5-ARYLAMINO-2-[N-(2'-MERCAPTOACETYLAMINO-4'-ARYLTHIAZOLO)]-THIADIAZOLES(III)

Sl. No.	R_1	R_2	Conc. used	% inhibition	I_{50} value
1.	4-CH_3	H	3.8×10^{-4}	80.13	2.3×10^{-4}
2.	H	H	3.8×10^{-4}	88.08	2.1×10^{-4}
3.	4-OC_2H_5	H	3.8×10^{-4}	40.41	4.7×10^{-4}
4.	2-OCH_3	H	3.8×10^{-4}	36.44	5.2×10^{-4}
5.	4-CH_3	Cl	3.8×10^{-4}	40.41	4.7×10^{-4}
6.	4-Cl	Cl	3.8×10^{-4}	99.70	1.9×10^{-4}
7.	4-Br	Cl	3.8×10^{-4}	85.10	2.2×10^{-4}

Acknowledgement

The authors' thanks are due to the Head, Department of Chemistry, Lucknow University, Lucknow for providing laboratory facilities. Grateful acknowledgement is made to Mr. F. A. Khan (SRF) for his help during AChE screening. One of us (M.G.) is thankful to U.P.S.C.S.T. for the award of a J.R.F.

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Leucoanthocyanidins from *Saraca asoca* Stem Bark

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Manuscript received 21 February 1980, revised 17 July 1980, accepted 7 August 1980

S. asoca (Ashoka : N. O. Leguminoseae) is well known for its medicinal properties. Its highly astringent stem bark is used in uterine affections in menorrhagia and scorpion sting[1]. In the past, some chemical constituents have been reported to be present in this bark[2,3,4]. The bark was extracted with acetone at room temperature and the concentrated viscous mass was subsequently macerated with petroleum ether, ethyl acetate, acetone and methanol respectively.

The light petroleum extracted some waxy matter along with β-sitosterol. The ethylacetate extract on fractional precipitation with light petrol yielded a homogeneous compound (A). The acetone fraction on column chromatography on silica gel afforded compound (B), methanol fraction on repeated crystallisation with methanol-ethyl acetate yielded a homogeneous entity (C).

From a study of colour reactions, UV spectral data, acid hydrolysis, degradation, co-chromatography, mp, mmp compound (A) $C_{21}H_{24}O_{11}$ was identified as leucopelargonidin 3-*O*-β-D-glucoside by the well known procedure[5,6]. Compound (B) $C_{15}H_{14}O_6$ was found to be identical with leucopelargonidin[7] and compound (C) $C_{15}H_{14}O_7$ with leucocyanidin[7].

The high astringency of the bark can be ascribed to the presence of these flavan-diols, and to the highly water soluble glycoside.

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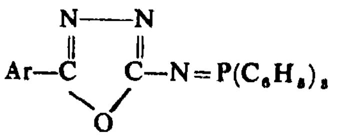
Studies on Heterocyclic Primary Amines. III : Synthesis of N-(5-aryl-1,3,4-oxadiazol-2-yl) Triphenyl Imidophosphoranes

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Manuscript received 24 January 1980, revised 5 May 1980 accepted 7 August 1980

IMIDOPHOSPHORANES in which the nitrogen atom is attached to heterocyclic ring are rare. Because of the increasing biological[1-6] and industrial[7] uses of 1,3,4-oxadiazole derivatives, we became interested in the preparation of new types of 1,3,4-oxadiazolylimidophosphoranes(I).



(I)

Ar

a = C_6H_5, b = *m*-ClC_6H_4, c = *p*-ClC_6H_4, d = *p*-$CH_3C_6H_4$, e = *p*-$CH_3OC_6H_4$

The synthetic route which was found to be most convenient for the desired heterocyclic imidophosphoranes(I) employed the method of Horner and Oediger[8]. Thus, on subjecting 2-amino-5-aryl-1,3,4-oxadiazole to dibromotriphenylphosphorane in dry benzene in the presence of triethylamine, at room temperature followed by four hours' reflux under nitrogen, the desired imidophosphoranes(I) were obtained in 70-80% yield.

The i.r. spectra of all the compounds(I) showed a band at about 1300 cm^{-1} due to the N=P stretching vibration[9a] with the concomitant disappearance of the NH stretching vibration at 3140 cm^{-1} present in the starting aminooxadiazoles. The P–C (aromatic) stretching absorption was observed for all the compounds at 1440 cm^{-1}[9b]. The i.r. spectra of all the compounds(I) also showed the cyclic C=N stretching bands at 1640-1690 cm^{-1}.

The structure of the imidophosphoranes was further confirmed by hydrolysis. When compounds (I) were refluxed with dilute HCl for three hours, gave the parent aminooxadiazole hydrochloride and triphenylphosphine oxide, identified by mixed m.p. and comparison of the i.r. with an authentic.

Experimental

Infrared spectra were determined in KBr pellets on Beckman IR-5A unit. All melting points are uncorrected.

The key starting 2-amino-5-aryl-1,3,4-oxadiazoles were obtained by oxidative cyclisation of aldehyde semicarbazones[10].

N-(5-aryl-1,3,4-oxadiazole-2-yl)triphenylimidophosphoranes(I) :

A well stirred suspension of dibromotriphenylphosphorane (1 m.mol) in 30 ml dry benzene was treated slowly (30 min) with a solution of aminooxadiazole (1 m.mol) and triethylamine (1 m.mol) in 30 ml dry benzene. The mixture was stirred at room temperature for 1 hr and then refluxed for four hrs. The precipitated triethylamine hydrochloride was removed by filtration. The solvent was removed under vacuum and the residue crystallised from benzene.

Table 1 represents the physical and analytical data of (I).

TABLE 1 – TRIPHENYLIMIDOPHOSPHORANES(I)

No.	R	m.p. °C	Formula	Microanalysis Calcd. %N	Found
Ia§	H	170-172	$C_{26}H_{20}N_3OP$	9.97	9.85
Ib	*m*-Cl	188-190	$C_{26}H_{19}ClN_3OP$	9.22	9.14
Ic	*p*-Cl	207-208	$C_{26}H_{19}ClN_3OP$	9.22	9.32
Id	*p*-CH$_3$	176-178	$C_{27}H_{22}N_3OP$	9.65	9.53
Ie§	*p*-CH$_3$O	200-201	$C_{27}H_{22}N_3O_2P$	9.31	9.18

§ The composition of Ia and Ie was also checked by analysis for phosphorus.
Ia, Calcd. P, 7.36 Found 7.50.
Ie, Calcd. P, 6.87 Found 7.00.

Hydrolysis of N-(5-aryl-1,3,4-oxaaiazole-2-yl)triphenylimidophosphoranes(I) :

Imidophosphoranes(I) (1 gm) was refluxed for three hours with dilute HCl (30 ml), then cooled and extracted with benzene. The benzene solution was washed with water and dried over sodium sulfate. Upon evaporation of benzene, triphenylphosphine oxide was obtained (70%), identified by mixed m.p. and comparison of the infrared with an authentic.

The parent aminooxadiazoles were obtained from the acidic solution by neutralisation with sodium hydroxide.

Acknowledgement

The authors are greatly indebted to Professor Dr. Samiha Abdel Wahab, Dean of the University College for Women, Ain-Shams University, Heliopolis, Cairo, for her helpful discussions and for providing all the facilities.

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Stereochemistry and Anti-inflammatory Activity of Carboxymethoximes of Ketones†

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Manuscript received 31 May 1979, accepted 7 August 1980

DURING the course of an investigation of carboxymethoximes as anti-inflammatory agents, Dijk and Zwagemakers[1] reported the anti-inflammatory activity of a number of oxime ether derivatives. The observations concerning the stereochemistry and the anti-inflammatory activity of carboxymethoximes of ketones made in this laboratory are recorded in this communication.

Reaction of the oximes of various ketones with monochloroacetic acid in presence of sodium hydroxide in aqueous alcohol yielded the *o*-alkylated derivative as was evident from the fact that identical compounds were also obtained when the ketones were reacted with 2-(aminooxy)acetic acid hemihydrochloride (Fig. 1). The assignment of the

† CDRI Communication No. 2522.

TABLE 1—PMR AND BIOLOGICAL DATA OF VARIOUS CARBOXYMETHOXIMES

Compd. No.	m.p. (°C)	Diagnostic PMR Data (δppm)	Molecular formula	Elemental analysis (%) Required	Found
1	2	3	4	5	6
1E	136-7	$CDCl_3$, 3.66, 3.72 and 3.78 (3S, 3×OCH_3), 1E+11.1 mg Eu(fod)$_3$, 3.69, 3.72 and 3.78 (3S, 3×OCH_3)	$C_{16}H_{17}NO_4$	C 66.89 H 5.96 N 4.87	66.72 5.84 4.91
1Z	115-7	$CDCl_3$, 3.58 (S, 2-OCH_3), 3.78 (S, 2×OCH_3), 1Z+10.5 mg Eu(fod)$_3$, 3.75 and 3.76 (2S, 2×OCH_3), 3.88 (S, 2-OCH_3)	$C_{16}H_{17}NO_4$	C 66.89 H 5.96 N 4.87	67.20 6.04 4.68
2E	Oil	CCl_4, 3.63, 3.71 and 3.76 (3S, 3×OCH_3), 4.46 (S, N−OCH_2)	$C_{18}H_{19}NO_6$	C 61.60 H 5.55 N 4.06	62.36 5.78 4.16
3E	Oil	CCl_4, 3.59 and 3.72 (2S, 2×OCH_3), 4.38 and 4.44 (broad d, −$OCH_2CH=CH_2$ and N−OCH_2 resp), 5.08-5.37 (m, $OCH_2CH=CH_2$), 5.72-6.08 (m, $OCH_2-CH=CH_2$)	$C_{20}H_{21}NO_6$	C 64.68 H 5.70 N 3.77	64.82 5.47 4.06
4E	84-5	CCl_4, 2.28 (S, CH_3), 3.59 (S, OCH_3) and 4.47 (S, N.OCH_2)	$C_{17}H_{17}NO_4$	C 68.22 H 5.72 N 4.68	68.47 5.95 4.56
5	104-5	$CDCl_3$, 3.44 and 3.68 (2S, 2×CH_2Ph), 4.78 (S, N−OCH_2)	$C_{17}H_{17}NO_3$	C 72.07 H 6.05 N 4.94	72.30 6.34 4.68
6Z	93-4	$CDCl_3$, 1.90 (m. Ph−$CH_2-CH_2-CH_2$−), 2.80 (q, Ph−$CH_2-CH_2-CH_2$−), 4.78 (S, N−OCH_2) and 7.95 (q, Ha, J=9 and 2Hz)	$C_{12}H_{13}NO_3$	C 65.74 H 5.98 N 6.39	66.10 6.24 6.15
7E	78-80	$CDCl_3$, 1.80 (S, −C−CH_3), 3.42 (S, Ph−CH_2) and 4.65 (S,N−OCH_2)	$C_{11}H_{12}ClNO_3$	C 54.66 H 5.00 N 5.79	54.95 4.70 5.91
8E	118-20	CCl_4, 1.70 (S,C−CH_3), 2.77 and 2.90 (2d, one methylene proton), 3.18-3.64 (two sets of multiplets, Ph−CH− and one methylene proton) and 4.50 (S,N−OCH_2)	$C_{18}H_{18}ClNO_3$	C 65.16 H 5.46 N 4.22	65.31 5.67 4.35
9E	Oil	CCl_4, 0.72 (t, CH_2-CH_3), 1.63-3.67 (m, showing CH_2CH_3, −$CHCH_2$Ph, PhCH−C=N−) and 4.55 (S, N−OCH_2)	$C_{19}H_{21}NO_3$	C 73.29 H 6.80 N 4.50	73.52 7.12 4.44
10E	Oil	CCl_4, 0.83 (t, CH_2CH_3), 1.90 (q, CH_2CH_3), 2.23 (S, CH_3), 2.68-2.84 (2d, one methylene proton), 3.1-3.6 (two sets of m, Ph−CH and one methylene proton) and 4.50(S,N−OCH_2)	$C_{20}H_{23}NO_3$	C 73.82 H 7.12 N 4.30	73.94 7.50 4.50
11E	Oil	CCl_4, 0.70 (t, CH_2CH_3), 1.68-3.33 (m, CH_2CH_3, PhCH_2−CH− and Ph−CH−C=N−), 3.57 and 3.62 (2S, 2×OCH_3), 4.53 (S,N−OCH_2)	$C_{21}H_{25}NO_5$	C 67.91 H 6.78 N 3.77	68.24 7.12 3.60
12E	72-74	CCl_4, 1.70 (S,C−CH_3), 2.24 (S, CH_3), 2.75 and 2.90 (2d, one methylene proton), 3.15-3.64 (two sets of multiplets, Ph−CH and one methylene proton) and 4.50(S,N−OCH_2)	$C_{19}H_{21}NO_3$	C 73.29 H 6.80 N 4.50	73.35 6.59 4.49
13E	Oil	CCl_4, 1.73 (S,C−CH_3), 2.85 and 3.0 (2d, one methylene proton) 3.33-3.80 (two sets of multiplets Ph−CH and one methylene proton) and 4.50 (S,N−OCH_2)	$C_{18}H_{18}ClNO_3$	C 65.16 H 5.46 N 4.22	65.50 5.75 4.28
14E	Oil	CCl_4, 0.85 (t, CH_2CH_3), 1.59-2.35 [m, Ph−CH−$(CH_2)_2$−Ph], 2.55 (q, CH_2CH_3), 3.35 (t. Ph−CH−) and 4.47 (S,N−OCH_2)	$C_{21}H_{25}NO_3$	C 74.31 H 7.42 N 4.13	74.30 7.72 4.43

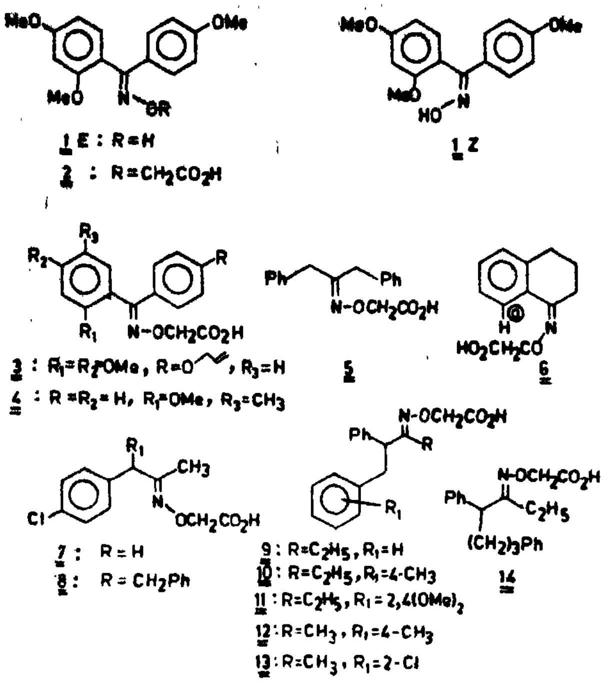


Fig. 1

stereochemistry of various carboxymethoximes was made on the basis of their PMR spectra. On the basis of the deshielding effect experienced by either alkyl or aromatic protons due to the magnetic anisotropic effect of $-NOCH_2$ group[2], the stereochemical assignment was made and are recorded in Table 1. Although Dijk and Zwagemakers[1] reported the predominant formation of the E-isomer of oxime and oxime-ethers of a large number of phenyl ketones, even than the PMR spectra of the E and Z-isomers of **1** were studied in presence of the $Eu(fod)_3$ as the shift reagent. The two isomers of **1** were separated by column chromatography of the isomeric mixture of the oxime (E : Z : 8 : 1) which was prepared by conventional method. The predominant E-isomer failed to exhibit any deshielding effect of the methoxy signal at position-2 (2 Hz), while in the Z-isomer this methoxy signal showed a considerable shift (21 Hz) in the presence of $Eu(fod)_3$. The stereochemical assignment of **6** was made on the basis of the chemical shift of the aromatic protons which were shown by Buchler[2] earlier to be of diagnostic value for stereochemical assignment. The stereochemistry of **7** was ascertained on the basis of comparative PMR studies with **5**. The two different chemical shifts of the two benzylic methylene protons in **5** indicated the magnetic anisotropic effect of the $-N-OCH_3$ group. Since the benzylic $-CH_2$ in **7** appeared at 3.42 δ, the E-configuration of the compound became evident. The configuration of **8-14** was studied on the basis of the chemical shift of $-NOCH_2CO_2H$ protons. In carboxymethoxime of *p*-chloroacetophenone, the E-configuration of which was proved by X-ray crystallographic studies[1], the $-OCH_2CO_2H$ protons appeared at 4.58δ. On the other hand, the chemical shift of the same $-NOCH_2CO_2H$ protons in **5** and **6** appeared at 4.78δ which indicated that in the E-configuration the alkyl group had a shielding influence on the $-NOCH_2CO_2H$ protons. Since the latter protons in **8-14** appeared at around 4.5δ, the E-configuration of these compounds became obvious.

Besides the configurational problem the carboxymethoximes possess a conformational problem also, as would be evident from the fact that the carboxymethoxime of *p*-chloroacetophenone in the solid state exists in a conformation in which the oxime ether function lies in a plane making an angle of 25° with the phenyl ring and the carboxyl function is almost perpendicular to the oxime ether grouping[7]. In the gaseous phase the conformation of the same compound allows the carboxyl group to be directed towards the N-atom. It would, therefore, be logical to expect that a complex carboxymethoxime like **8**, would possibly exist in different conformations in solution. The PMR spectra of **8**, the purity of which was meticulously checked by high pressure liquid chromatography, at 300 MHz exhibited two signals for $-CH_3$ and $-NOCH_2$ protons at δ 1.77, 1.78 and 4.69, 4.70 respectively. Since, such a minor difference in chemical shift can only arise because of different conformations in solution, it became obvious that **8** in solution existed in more than one conformations.

Anti-inflammatory Activity :

All the compounds were tested in albino mice (18-22 g) for toxicity. The anti-inflammatory activity was also tested in mice (18-22 g) of either sex at 1/5th of LD_{50} doses. Graded doses of the compound were administered intraperitoneally to groups of five mice in order to ascertain the acute toxicity. The animals were observed continuously for 2 hr and mortality was noted after 24 hr. The approximate LD_{50} (ALD_{50}) was calculated from mortality observed in different groups. Anti-inflammatory activity was evaluated against carrageenin induced oedema in mice following the procedure of Srimal and Dhawan[8]. One hour after the oral feeding of the compound, carrageenin 1% solution was injected into the left paw of the animals. The effect of the compound was assessed 4 hr after the injection of the carrageenin. Percentage inhibition of carrageenin induced oedema exhibited by 3E, 5 and 8 were 30, 44 and 28% respectively.

Experimental

General method of the alkylation of oximes : A mixture of the appropriate oxime (0.01 mol), monochloroacetic acid (0.013 mol) and NaOH (0.03 mol) in aqueous alcohol (25 ml) was refluxed for 18-20 hrs. After the completion of the reaction, the solvent was distilled off under vacuo and the

residue extracted with ethyl acetate to remove the unreacted starting oxime. The aqueous layer was made acidic with dil. aq. HCl to yield the desired carboxymethoximes (40-90%).

Reaction of ketones with 2-(aminooxy)acetic acid hemihydrochloride : A solution of appropriate ketone (0.01 mol), 2-(aminooxy)acetic acid hemihydrochloride (0.01 mol) and sodium acetate (0.03 mol) in ethanol (60 ml) was refluxed for 18-20 hrs. The solvent was removed under vacuo, and the residue extracted with ethyl acetate. The organic layer was washed with water, dried over anhydrous sodium sulphate and concentrated to yield the desired carboxymethoximes (40-90%).

Acknowledgement

Thanks are due to Dr. Y. P. Gavrilov of Shemyakin Institute of Bioorganic Chemistry, U.S.S.R. Academy of Sciences, Moscow for the 300 MHz PMR spectrum of one of the compounds, Dr. I. M. Chak for LD_{50} data and Mrs. U. Sharma for technical assistance.

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Flavonoids of *Ipomoea dissecta*

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Manuscript received 27 May 1980, revised 19 August 1980, accepted 29 October 1980

IPOMOEA dissecta[1] Willd. [syn. *I. coptica* (L.) Roth.] belonging to the Convovulaceae is reported to contain chlorogenic acid in the leaves[2]. *I. fistulosa* has been recorded to contain kaempferol in the flowers[3] and β-sitosterol in the leaves[4]. We now report the chemical components of the flowers of *I. dissecta*.

Fresh flowers (75 g) of *I. dissecta* collected from the Regional Engineering College Campus, Tiruchirapalli during late winter were extracted with hot 80% EtOH under reflux and the combined extract concentrated *in vacuo* and the aqueous concentrate fractionated successively into petrol (60-80°), ether and ethylacetate (EtOAc) solubles. The petrol fraction did not yield any crystalline solid.

The residue (0.1 g) from the ether fraction on crystallisation from Me_2CO yielded a yellow solid (0.06 g) m.p. 277-79°, ~~tetraacetate, m.p. 185-87°~~ and was identified as kaempferol by R_f, colour reactions, uv and direct comparison with an authentic sample.

The residue (0.05 g) from the EtOAc fraction was dissolved in methanol and was subjected to preparative PC (Whatman No. 3, 15% HOAc) and the methanolic eluate of the only band that separated had λ_{max}(MeOH) 243 (sh), 251 (sh), 268, 323 (sh), 365 nm ; Δλ (NaOMe)+50 nm ; Δλ ($AlCl_3$) and Δλ ($AlCl_3$/HCl)+59 nm ; Δλ (NaOAc) nil (band II) and Δλ (NaOAc/H_3BO_3) nil and responded to all the reactions expected of a flavone glycoside. It could be hydrolysed easily with 7% H_2SO_4 (100°, 2 hr) to yield kaempferol and glucose in almost equal quantities. The glycoside could therefore be identified as kaempferol-7-glucoside by R_f and uv data and the identity confirmed by direct comparison with an authentic sample.

This appears to be the first record of isolation of kaempferol and its 7-glucoside from *I. dissecta*.

Acknowledgement

Our thanks are due to the Head of the Department for his continued interest and encouragement.

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Antibacterial and Antialgal Activity of N-Isonicotinylamido-N'-Aryl/Guanidines

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and

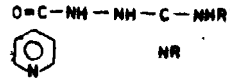
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Manuscript received 5 November 1977, revised 12 June 1978, accepted 29 October 1980

CERTAIN alkyl/aryl guanidines or diaryl guanidine derivatives of isonicotinic acid hydrazide have been prepared with a view to evaluating their antibacterial activity. Isonicotinic acid hydrazide has been reacted with aryl amidine chlorides[1] in chloroform solution of the respective arylcyanamide[2] to afford hydrochloride salts (I and II). The

TABLE—N-ISONICOTINYL-N′, N″-ARYL/ALKYL GUANIDINES



Sl. No.	R	R″	Mol. Formula*	M. P. °C	Picrate m.p. °C	% yield	I. R. frequencies (cm^{-1})
1.	2.	3.	4.	5.	6.	7.	8.
1	H	C_6H_5	$C_{13}H_{14}N_5OCl$	109	148	91	3250w (NH) ; 1680s −CONH ; 1620s and 1590m guanidine, 840s guanidine
2	H	o-$CH_3C_6H_4$	$C_{14}H_{17}N_5OCl_2$	232	215	85	3200m NH ; 1680s −CONH ; 1620-1600m guanidine, 860, guanidine
3	H	m-$CH_3C_6H_4$	$C_{14}H_{16}N_5OCl$	170	222	89	3450m NH ; 1650s −CONH ; 1620m and 860w guanidine
4	H	p-$CH_3C_6H_4$	$C_{14}H_{17}N_5OCl_2$	195**	125	83	
5	H	m-ClC_6H_4	$C_{13}H_{14}N_5OCl_2$	215	175	90	3300w NH, 1700m −CONH, 1660−1620 and 850s guanidine ; 710w C−Cl
6	H	p-ClC_6H_4	$C_{13}H_{14}N_5OCl_2$	175	180	87	3375m NH ; 1740s −CONH ; 1680s and 820 guanidine, 760w C−Cl
7	H	n-Butyl	$C_{11}H_{8}N_5OCl$	250(d)	–	82	
8	H	Isopropyl	$C_{10}H_{16}N_5OCl$	250(d)	–	80	
9	C_6H_5	C_6H_5	$C_{19}H_{17}N_5OCl$	206	–	75	
10	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	$C_{21}H_{21}N_5O$	165	–	78	
11	m-$CH_3C_6H_4$	m-$CH_3C_6H_4$	$C_{21}H_{21}N_5O$	195	–	86	
12	o-$CH_3C_6H_4$	o-$CH_3C_6H_4$	$C_{21}H_{22}N_5OCl$	236	–	88	3250m −NH ; 1060s, N−C(=N)−N , 1580s, 1620s, N−C=N , 1620s CO ; 2527s, $NH_2^+Cl^-$
13	p-ClC_6H_4	p-ClC_6H_4	$C_{19}H_{16}N_5OCl_3$	223	–	76	3250m NH[4] ; 1082s, N−C(=N)−N ; 1590w, N−C=N , 1630wCO

* The analytical data are within the admissible limits of experimental error.
** Hygroscopic.

alkylcyanamides and diaryl carbo-diimides were reacted with isoniazid. After refluxing the contents for one hour, dry hydrogen chloride gas was passed when respective guanidine hydrochlorides were obtained. These were characterised by elemental analysis and IR spectra.



I II

Where R=Alkyl or aryl groups Ar = aryl groups

The compounds were tested for antibacterial activity against *E. coli, Kleibsiella, pneumonae, Aeromonos hydrophila, Staphyllococcus aureus, Streptococcus faecalis, Proteus mirabilis* and *Proteus vulgaris* and were found inactive at a conc. of 200 μg/ml. In a test for inhibition of growth of the blue-green alga *Anacystis nidulans*, *o*-Tolyl derivative (2, Table 1) exhibited the greatest activity and inhibited its growth at a conc. or 10 μg/ml.

(1) Preparation of N-Isonicotinylamido-N′-alkyl/N′, N″-diaryl Guanidines :

The required alkyl cyanamides/1, 3-diaryl carbodiimides were obtained by complete desulfurisation of corresponding alkyl or 1,3-diaryl thiocarbamides with yellow lead oxide in acetone on a water-bath for about one hour. The black lead sulphide was filtered. The filtrate containing alkyl cyanamide/1, 3-diaryl carbo-diimide was treated with equivalent amount of isonicotinic acid hydrazide and dry hydrogen chloride gas was passed for 5 minutes. A solid separated out which was filtered and gave the expected products. These were recrystallised from ethanol. These results are presented in the Table.

(2) Preparation of N-Isonicotinylamido-N′-Aryl Guanidines :

The aryl amidine chlorides were prepared by passing dry hydrochloric acid gas in chloroform solution of the respective aryl cyanamide. These were obtained by desulfurisation of aryl thiocarbamides with lead acetate in alkaline medium. The lead sulphide was filtered off and the alkaline filtrate was neutralised with cold glacial acetic acid. The precipitated cyanamide was extracted with chloroform. Isoniazid dissolved in acetone was added. In some cases the reaction products were obtained immediately, while in others refluxing of the reaction mixture for half an hour was necessary to complete the reaction. The products were filtered, dried and m.p. determined. Picrates were

prepared from their aqueous or ethanolic solutions. The results are summarised in Table.

Acknowledgement

The authors wish to thank authorities of Institute of Technology for the facilities, Prof. P. C. Sen, Head, Deptt. of Microbiology, Institute of Medical Sciences for antibacterial testing, to Dr. A. K. Kashyap, Lecturer, Department of Botany for antialgal testing, to microanalytical section, Chemistry Department for microanalysis and I. R. Spectra, and the U. G. C. and C. S. I. R., New Delhi, for the award of Research Fellowships to Man Raj and Rajendra Singh respectively.

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Composition of Essential Oil of *Thymus serpyllum* Linn.

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Manuscript received 25 January 1980, accepted 29 October 1980

THYMUS serpyllum Linn., widely distributed in Kumaon region of U. P. between 1600 and 3000 m. is used indigenously against the complaints of stomach, liver, kidney and vision. The work, so far, reported on essential oil of *Thymus serpyllum* shows that the chemical composition varies depending on the extrinsic factors[1-3]. The authors[4] earlier reported 17 compounds viz., α-pinene, camphene, β-pinene, car-3-ene, α-terpinene, limonene, 1,8-cineole, γ-terpinene, *p*-cymene, terpinolene, *trans*-β-tepineol, terpinen-4-ol, geraniol, traces of citronellal and linalool, thymol and carvacrol besides 6 unidentified compounds in the oil extracted from young plant material of *Thymus serpyllum*. The present communication relates to the analysis of the essential oil of fully matured plant to get detailed knowledge of the volatile constituents and to find out the change in composition of the oil in different seasons.

The essential oil was extracted from fresh plant material by steam distillation. The oil was separated from the distillate with pet. ether (60-80°), dried over anhydrous sodium sulphate and solvent was distilled off. Pet. ether solution of the oil (5 g) was treated with aq. sodium hydroxide (5%). The aqueous layer was separated, neutralized and extracted with ether. The phenols (3.1 g) were recovered by evaporating the solvent[4]. The phenolic mixture was cooled and the crystals formed were separated. The solid and liquid phenols were purified, their characteristic derivatives prepared and were identified as thymol (phenylurethane m.p. 106° ; 3,5-dinitrobenzoate m.p. 102.5°) and carvacrol (phenylurethane m.p. 134° ; 3,5-dinitrobenzoate m.p. 76°) respectively.

The oil free from phenols was analysed using the combined GC – MS instrument under the following conditions :

A 25 meter glass capillary column (i.d. 0.3 mm) coated with FFAP in Carlo Erba 2300 gas chromatograph was coupled with JEOL JMS – D 300 mass spectrometer through the glass interface which was further attached to JMA-2000 data system. 0.3μl of the sample was injected (injection split ratio 1 : 100). The column temperature was maintained at 60° for first six minutes, raised to 100° and then programmed at 4° per minute upto 180°. The injection, interface and ion source temperatures were 250°, 220° and 230° respectively. The ionization energy used was 70 ev. The spectra were scanned at 2.5 seconds interval. The reconstructed total ion chromatogram and mass spectra were plotted by the computer.

The chromatogram of the oil is presented in the Figure. The compounds corresponding to the peaks,

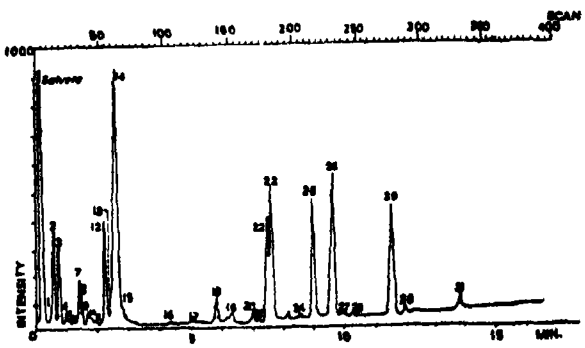


Fig. Gas chromatogram of *Thymus serpyllum* Oil

identified by their mass spectra and GC, are given in the Table.

The phenols are the principal constituents of the oil (thymol 60% and carvacrol 2%). The monoterpene hydrocarbons, sesquiterpene hydrocarbons, alcohols, esters and ketones constituted 18%, 7%, 8%, 2%, and 2% of the oil respectively. Terpinen-4-ol and *trans*-β-terpineol were found to be absent in the oil from the matured plant and the percentage

TABLE: CONSTITUENTS OF ESSENTIAL OIL OF *Thymus Serpyllum*

GC Peak	Compound	GC Peak	Compound
1.	α-Thujene	17.	α-p-Dimethylstyrene
2.	α-Pinene	18.	*trans*-Sabinene hydrate
3.	Camphene	19.	Camphor
4.	β-Pinene	20.	*cis*-Sabinene hydrate
5.	Sabinene	21.	Bornyl acetate
6.	Car-3-ene	22.	Caryophyllene
7.	Myrcene	23.	Thymyl methyl ether
8.	α-Terpinene	24.	Humulene
9.	Limonene	25.	Borneol
10.	β-Phellandrene	26.	β-Bisabolene
11.	1 : 8-Cineol	27.	δ-Cadinene
12.	γ-Terpinene	28.	Sesquiterpene ($C_{15}H_{24}$)
13.	Octan-3-one	29.	Thymyl acetate
14.	p-Cymene	30.	Carvacryl acetate
15.	Terpinolene	31.	Sesquiterpene alc. ($C_{15}H_{24}O$)
16.	Nonan-3-one		

of phenols was higher (62%) than that from the young plants (48%). Thus, the composition of the oil from the fully matured plant is considerably different from that of the young plant material.

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ERRATA

J.I.C.S. LVII, April 1980, pp. 398-401

Paper entitled 'An Equation for the.........0.1N by B. N. Ghosh

In the last para of page 401, please *read*

$e/2L^2(2\pi ax)$ *for* $e/L^2(2\pi ax)$;
$2L^2(2\pi a)$ *for* $L^2(2\pi a)$;
$0.96e/2L^2(2\pi a)$ *for* $0.96e/L^2(2\pi a)$

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